TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition

of

Реакционная способность органических соединений

Vol. XVI

ISSUE 2(58)

September 1979

TARTU

TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition

of

Реакционная способность органических соединений

Vol. XVI

ISSUE 2(58)

September 1979

TARTU

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ. Том XV. Выпуск 2(58). Сентябрь 1979. На английском языке. Тартуский государственный университет. ЭССР, г. Тарту, ул. Кликооли, 18. Ответственный редактор В. Пальм. Сдано в печать 01/10 1979. Бумага печатная 30x42 1/4. Печ.листов 8,75 (условных 8,14). Учетно-издат. листов 7.23. Тираж 400. Типография ТГУ, ЭССР, г. Тарту, ул.Пялсона, 14. Зак. № 1339. Цена 1 руб. 10 коп.

C O N T E N T S

Deuterium Isotope Effect in the Reactions of Activated Benzenesulfonic Acid Derivatives with Butylamine in Benzene

R. Vizgert and S. Sheiko

Donetsk Polytechnical Institute

Received February 28, 1979

Kinetic isotope effect in the reactions of activated benzene derivatives $(CF_3SO_2)_2C_6H_3X$ at $X=SO_2NHC_6H_5$, SO_2Cl, SO_2F,Cl with butylamine has been studied with the substitution of deuterium for hydrogen atoms. The decomposition mechanism of an intermediate of zwitter-ion type in the non-catalytic and catalytic reactions is discussed.

It has been shown in Ref. 1 that reactions of benzenesulfonic acid derivatives activated by two trifluoromethane sulfonic groups are the subject to the general basic catalysis by a second amine molecule. In this connection we suggested that a rate-determining step should be a decomposition of an intermediate which can proceed both via non-catalytic and catalytic path. In order to clarify the decomposition mechanism the isotope effect was studied with the substitution of deuterium for hydrogen atoms in the amino groups of butylamine in the reactions with $(CF_3SO_2)_2C_6H_3X$ at $X=SO_2NHC_6H_5$ (I), SO_2Cl (II), SO_2F (III), and Cl (IV).

Measurement of the arylation kinetics of N,N-dideuterobutylamine has revealed that as in the case of butylamine the reaction of compound (IV) is non-catalytic and those of compounds (I-III) are hindered by the second amine molecule catalysis. The observed rate constants depend linearly on the concentration of N,N- dideuterobutylamine (Fig.1 a,b).

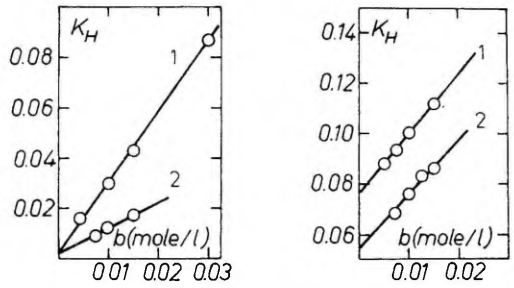


Fig.1. The observed rate constants vs. concentration of butylamine (1) and N,N - dideuterobutylamine (2) in the reactions:

a) with compound (I)

b) with compound (III)

This dependence can be expressed by the equation:

$$k_{obs} = k_o + k_b\, b$$

where k_{obs} is the observed rate constant, k_o ($l.mol^{-1}.sec^{-1}$) and k_b($l^2.mol^{-2}.sec^{-1}$) are non-catalytic and catalytic rate constants, respectively, b(mol/l) is the concentration of butylamine and N,N-dideuterobutylamine.

The Table lists k_o and k_b for reactions of compounds (I-IV) with butylamine and its deuterium analogue in benzene and also the ratios k^H/k^D which are a quantitative measure of the isotope effect. One can see that for the reaction of compound(I) with butylamine the ratio k_o^H/k_o^D is less than unity, i.e. in non-catalytic reaction primary isotope effect is absent. Small acceleration of the reaction can be accounted for by the increase in basicity of butylamine due to the higher electron-donating properties of deuterium atoms over hydrogen ones[2].

For a catalytic reaction the ratio $k_b^H/k_b^D = 2.94$. This indicates the presence of a primary isotope effect resulting from the proton ejection and transfer in the rate limiting step. This agrees with the obtained for this reaction general basic catalysis mechanism with different organic bases.

Table

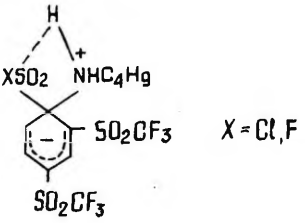
Values of Rate Constants and Isotope Effects of the Reactions of Activated Benzene Derivatives $(CF_3SO_2)_2C_6H_3X$ with Butylamine and its N,N-Dideuterium Analogue in Benzene.

X	$k_o^H \cdot 10^2$	k_b^H	$k_o^D \cdot 10^2$	k_b^D	k_o^H/k_o^D	k_b^H/k_b^D
			50°C			
	*0.228±	*2.77±	0.253±	0.942±	0.91	2,94
$SO_2NHC_6H_5$	0.022	0.01	0.054	0.001		
			40°C			
	**13.88±	**6.99±	12.49±	2.35±	1.11	2.97
SO_2Cl	0.29	0.27	0.27	0.44		
			40°C			
	**7.51	**2.41±	5.47±	2.20	1.37	1.09
SO_2F	0.21	0.21	0.28	0.24		
			40°C			
	**6.22±		6.43		0.97	
Cl	0.13		0.15			

*Determined in Ref.1

**Determined in Ref.3

In the reactions of compounds (II) and (III) with butylamine primary isotope effect was observed both in catalytic and non-catalytic reactions. The ratio k_o^H/k_o^D for compounds (II) and (III) equals 1.11 and 1.37, respectively. If the ejection of proton and amino group occurs in the limiting step, for the non-catalytic decomposition of an intermediate product a four-member cyclic transition state (where the ejection of a leaving group is favored by the formation of a hydrogen bond with an amino group proton) can be assumed (cf. Ref.4).

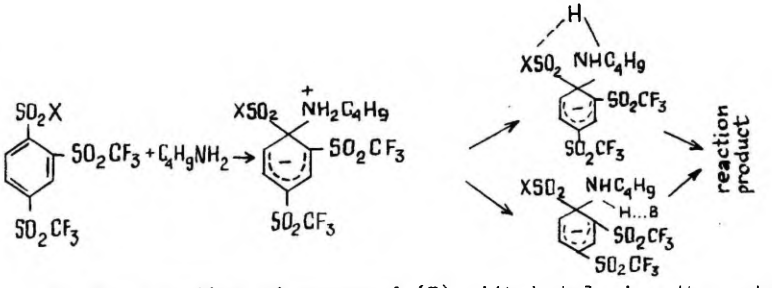


The ejection of leaving groups SO_2Cl and SO_2F is favored by an amino group proton. In this case the ratio k_b/k_o becomes equalled to 50.36 for compound (II) and 32.1 for compound (III). For compound (I) where the proton transfer in the non-catalytic reaction is absent, this ratio is 1214.9.

For the catalytic reactions of compounds (II) and (III) the values of k_b^H/k_b^D are 2.97 and 1.09, respectively.

They indicate the proton elimination in the rate limiting step.

Thus for compounds (II) and (III) the following reaction scheme can be suggested:



In the reaction of compound (I) with butylamine the rate determining step is an addition of nucleophile. Thus it is clear why the primary isotope effect was not observed by us.

Experimental

N,N- dideuterobutylamine was obtained by shaking (3 times) benzene solution of butylamine with heavy water containing 99.8% of deuterium, the water being changed each time.

The obtained benzene solution of deuterium butylamine was dried over anhydrous sodium sulfate during an hour . The deuterium content in the amino group of butylamine was determined by the IR spectra (Fig.2).

As one can see from this figure in deuterated amine the NH_2 group is absent, and NHD group is present in a small amount only. For the latter the maximum of the N-H bond vibration is at 3355 cm^{-1}. This is in agreement with the assumption from Ref. 3 according to which N-H bonds in NHD group should be located between symmetric and asymmetric stretching vibrations of the NH_2 group.

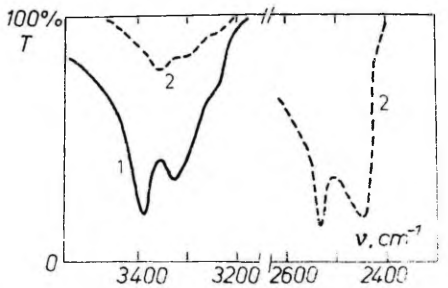


Fig.2. IR spectra: I-butylamine (0.15 M) and 2-N,N-dideuterobutylamine (0.2 M). The cell thickness is 0.05 cm.

According to the calculation (assuming that the apparent extinction coefficient of the N-H bond absorption maximum in the NHD group equals a half sum of the corresponding coefficients of symmetric and asymmetric vibrations of the NH_2 group) the deuterated product contained 86.6% of dideuterated amine and 13.4% of amine with NHD group (i.e. the amino group contained 94.3% of deuterium). The solutions

for kinetic measurements were prepared by diluting the obtained solution of N,N- dideuterobutylamine with an additional portion of benzene. To remove the traces of H_2O in the solvent benzene was treated with heavy water beforehand.

For the kinetic measurements and calculation of the rate constants see Ref. 1.

References

1. R.Vizgert and S.Sheiko, Zh.org.khim., to be published
2. L.Melander, Isotope Effects on Reaction Rates, M., "Mir", 1966, p.98 (Russ. transl.)
3. R. Vizgert and S. Sheiko, Organic Reactivity, to be published
4. L. Litvinenko, Y. Titsky, and A. Shumeiko, DAN Ukr. SSR, ser. B, N9, 804(1976)

LEAVING GROUP EFFECT IN THE REACTION OF ARYLATION OF BUTYLAMINE BY 2,4-BIS (TRIFLUOROMETHANE SULFONYL) BENZENESULFONIC ACID DERIVATIVES IN BENZENE

S. Sheiko and E. Mitchenko

Donetsk Polytechnical Institute,
Institute of Physico-Organic and Coal Chemistry,
Ac. Sci., Ukr.SSR

Received February 28, 1979

To elucidate the leaving group effects on the reaction of arylation of butylamine by 2,4-bis (trifluoromethane sulfonyl) benzenesulfonic acid derivatives the kinetics of reactions of $(CF_3SO_2)_2C_6H_3X$ (X=$SO_2NHC_6H_5$, SO_2F, SO_2Cl, and Cl) with butylamine in benzene at 40° is studied. The leaving group effect on the non-catalytic reaction and that catalyzed by butylamine is discussed.

It has been shown[1] that bimolecular reaction of arylation of butylamine by 2,4-bis (trifluoromethane sulfonyl) benzene sulfone anilide (I) is hindered by the catalysis by the second amine molecule. To elucidate the leaving group effect the present communication studies the kinetics of the reactions of compounds $(CF_3SO_2)_2$, C_6H_3X at X=SO_2F(II), SO_2Cl(III), Cl(IV) with butylamine in benzene at 40°C.

The observed rate constants for reactions with compounds (II) and (III) depend linearly on the concentration of butylamine (see Fig.1). This dependence can be expressed as :

$$k_{obs} = k_o + k_b b$$

where k_{obs} ($l.mol^{-1}\ sec^{-1}$) is the observed rate constant, k_o ($l\ .\ mol^{-1}.\ sec^{-1}$) and k_b($l^2.\ mol^{-2}.\ sec^{-1}$) are the rate constants of the non-catalytic reaction and that catalyzed by the second amine molecule respectively, b ($mol.l^{-1}$) is

the concentration of butylamine. The k_o and k_b values calculated by the least squares method are listed in Table 1.

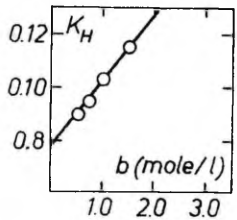


Fig. 1. Plot of the observed constants (k_{obs}) vs. concentration of butylamine in the reaction with 2,4-bis (trifluoromethane sulfonyl) benzene sulfonyl fluoride.

Table 1

The Leaving Group Effect on the Non-catalytic (k_o) and Catalytic (k_b) Reaction Rate Constants of $(CF_3SO_2)_2C_6H_3X$ with Butylamine in Benzene (40°C).

X	$k_o.10^2$ ($l \cdot mol^{-1} \cdot sec^{-1}$)	k_b ($l^2 \cdot mol^{-2} \cdot sec^{-1}$)
$SO_2NHC_6H_5$	* 0.228 ± 0.022	* 2.77 ± 0.01
SO_2F	7.51 ± 0.21	2.41 ± 0.21
SO_2Cl	13.88 ± 0.29	6.99 ± 0.27
Cl	6.22 ± 0.13	

* Determined in Ref. 1 at 50°C.

For the reactions with compound (IV) the observed second order rate constant is independent of the concentration of butylamine (see Table 2).

The general course of the reaction of this type can be represented by the scheme:

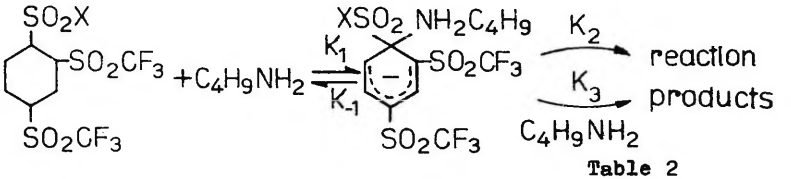


Table 2

The Butylamine Concentration Influence on the Arylation Rate Constant of Butylamine by 2,4-Bis (Trifluoromethane Sulfonyl) Chlorobenzene in Benzene (50°C)

b(mol . l^{-1})	k_{II} ($l.mol^{-1}.\ sec^{-1}$)
0.005	0.III ± 0.005
0.010	0.112 ± 0.002
0.015	0.115 ± 0.001

The application of the stability principle to this step scheme gives the equation describing the reaction rates of this type:

$$\frac{k_1 k_2 [ArX][B] + k_1 k_3 [ArX][B]^2}{k_{-1} + k_2 + k_3 [B]} \qquad (I)$$

Assuming that in this equation:

I) $k_2 + k_3 [B] \gg k_{-1}$, one can neglect k_{-1} and then the expression $v = k [ArX][B]$ can be obtained, i.e. the kinetics is determined by the formation of an intermediate product.

2) $k_2 + k_3 [B] \ll k_{-1}$, Eq. (2) results from Eq. (1):

$$v = k [ArX][B] + k' [ArX][B]^2 \qquad (2)$$

The third order term reflects the fact that the decomposition of an intermediate determines the reaction rate.

The presence of the catalysis and, hence, the realization of case 2 was observed for the leaving groups SO_2Cl,

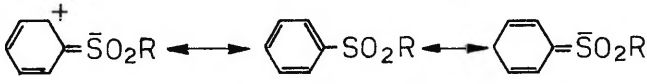
SO_2F, $SO_2NHC_6H_5$. Case I is realized for the leaving group Cl.

A reversal of the rate-limiting step in the case of 2,4-bis (trifluoromethane sulfonyl) benzene with transition from X=Cl (the formation of an intermediate product) to X = SO_2Cl, SO_2F, $SO_2NHC_6H_5$ (the decomposition of an intermediate is due to the fact that chlorine is a good leaving group and sulfonyl containing substituents are less favorable leaving groups.

As is known the criterion of a tendency to break a chemical bond is a bond energy, but we have no information about the C_{Ar}- S bond breaking energy. The information about the firmness of bonds can be also given by 1) electronegativity and volume of leaving groups 2) polarizability of bonds.

Due to the higher electronegativity of SO_2X groups (e.g., for SO_2Cl σ_J= 0.80)[8] the C_{Ar}- S bond is more polar over the C_{Ar} -Cl bond (σ_J=0.47)[9].

If in the $C_6H_5SO_2R$ molecule there occurs a mesomeric interaction accompanied by the shift of π-electronic density of the ring on the sulfonyl group according to the scheme [3,4]



it should also contribute into the increase in the electron density on the leaving group and growth of its mobility.

We have no information about the polarizability of bonds. Lower mobility of tne SO_2Cl, SO_2F, and $SO_2NHC_6H_5$ groups over chlorine is, probably, just to their larger volume which creates steric hindrances for the nucleophilic attack on the reaction center.

Judging about the reactivity of compounds (I-III) by the magnitude of the non-catalytic constant k_o, the compounds can be situated in the following order:

$SO_2Cl > SO_2F > SO_2NHC_6H_5$

When analyzing non-catalytic constants one can see that they are close for compounds (II) and (III) and differ considerably from the constant for compound (I). This may result from the formation of the transition states of cyclic type in the reactions of compounds (II) and (III) and the absence of such a transition state in the reaction of compound (I). Presence of the cyclic transition state favors the ejection of the leaving group in a non-catalytic reaction and equilizes non-catalytic constants of compounds (II) and (III).[6]

Suter[5] mentions about considerably lower mobility of a sulfonyl fluoride group over sulfonyl chloride one without discussing the causes. In the reaction studied sulfonyl fluoride group is also less mobile than sulfonyl chloride group. Comparing induction ($\sigma_{SO_2F} = 0.75$, $\sigma_{SO_2Cl} = 0.80$) and resonance ($\sigma_{SO_2F} = 0.26$, $\sigma_{SO_2Cl} = 0.24$) constants[8], we can draw a conclusion that the induction effect of the leaving group on the reaction center is stronger than mesomeric and thus the SO_2Cl group with the higher induction constant is more mobile.

In the case of a catalytic flow the nature of a catalyst (its ability to form hydrogen bonds with proton ejection from an intermediate product) plays the key role in the reaction course. Thus when analyzing the values of catalytic constants of arylation of butylamine by compounds (I-III), where in three cases all butylamine is a catalyst, one can see that the catalytic constants differ from each other insignificantly and are within the limits of the same order.

Table 3 lists the activation parameters of the reactions of arylation of butylamine by compounds (III) and (IV) determined by us.

Table 3

Rate Constants ($k_o \cdot 10^2$, l. $mol^{-1} \cdot sec^{-1}$) and Activation Parameters of the Reactions of $(CF_3SO_2)_2C_6H_3X$ with Butylamine in Benzene

X	20°	30°	40°	50°	IgA	E(kcal/mol	$\Delta S^{\neq}$, e.u.
Cl		3.88±	6.22±	11.5±	6.16	10.52	-32.1
		0.11	0.13	0.1			
SO_2Cl	8.21±	10.61±	13.88±		2.42	4.70	-54.1
	0.40	0.35	0.29				
	6.42±	6.59±	6.99±				
	0.36	0.32	0.27				

*Rate constants (k_b, $l^2 \cdot mol^{-2} \cdot sec^{-1}$) for the reaction of $(CF_3SO_2)_2C_6H_3SO_2Cl$ with butylamine catalyzed by the second butylamine molecule.

Activation parameters of compound (IV) are close to the literature ones for compounds $(NO_2)_2C_6H_3X$ at X=Cl,I, and Br [8]. This may be regarded as an indication to a common mechanism. The attention should be paid to the fact that with transition from compound (III) to compound (IV) entropy of the non-catalytic reaction falls.
This reflects the more rigorous steric requirements in the transition state of the reaction of compound (III), probably due to the formation of an intermediate of a cyclic type.

References

1. Vizgert and S. Sheiko, Zh. org.khim., to be published
2. H. Becker, Einführung in die Elektronentheorie Organisch-Chemischer Reaktionen, M., "Mir", 1977, p. 418 (Rus. transl.)
3. S. Oae, Chemistry of Organic Sulfur Compounds, " M., "Khimiya", 1975 (Rus.transl.)
4. Yu. Egorov, Yu. Borovikov, S. Vdovenko, V. Didkovsky,

V. Boiko, and Y. Shupak, Teor. i eksp. khim., 14, 84 (1978)
5. Ch.Suter, The Organic Chemistry of Sulfur, part II, M.IL, 1951, p.271 (Rus.transl.)
6. R. Vizgert and S. Sheiko, Organic Reactivity, 15, I45 1979
7. L. Litvinenko Y. Titsky, and A. Shumeiko, Zh. org.khim., 11, issue 5, 1011 (1977)
8. L. Yagupolsky, A. Ilchenko, and N. Kondratenko, Usp. khim., 43, issue I, 64 (1974)
9. A. Gordon and R. Ford, "Chemist's Companion", M., "Mir," 1976, p. 173 (Rus.transl.).

INFLUENCE OF ORGANIC COMPOUNDS ON THEIR HEATS OF MIXING WITH ANILINE AND ACETONE

R.G. Makitra and Ya.N. Pirig
Institute of Geology and Geochemistry of Fuels,
Acad. Sci. Ukr. SSR, Lvov

Received April 5, 1979

The values of the heats of mixing of aniline and acetone with organic compounds at the 1:1 ratio are satisfactorily described by linear five-parameter equations which take into account the polarizability, polarity, cohesion energy density, basicity, and electrophilicity of the second component as the correlated parameters.

Spectral basicities of compounds "B"[1] are proportional to their donor numbers DN, i.e. to their heats of mixing with a strong acceptor $SbCl_5$[2]. However, for the weaker acceptor $CHCl_3$ this proportionality is worse and a number of compounds, especially the associated alcohols, do not obey this linear dependence[2,3]. This is, probably, caused by the lower values of heats of mixing with $CHCl_3$ (< 1 kcal/mole) over DN (up to 30 kcal/mole) and, respectively, by the more marked influence of non-specific solvation effects which should be taken into account on the calculations. Thus a satisfactory correlation between the mixing heat effect values with $CHCl_3$ and the basicity "B" can be obtained only with taking into account the non-specific solvation phenomena by means of linear poly-parameter equation and providing that the associated and non-associated compounds are considered separately.

It was interesting to verify the applicability of the proposed calculation principle for other compounds. The sufficient for a mathematical treatment data on heats of

mixing for aniline and acetone are to be found in the literature[4]. These compounds are the more interesting, as, unlike $CHCl_3$, they are electron donors and, hence, their heats of mixing may be both positive and negative.

The values of mixing heats of aniline with some compounds[4] and their parameters - polarizability, polarity, cohesion energy density, basicity[1] and electrophilicity[5] are given in Table 1. With data handling for 20 points all by the linear five-parameter equation

$$\Delta H = A_0 + A_1 \frac{n^2 - 1}{n^2 + 2} + A_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + A_3 \delta^2 + A_4 B + A_5 E$$

only a low correlation coefficient R=0.921 which corresponds to a "poor correlation"[6] is obtained. But the mixing heats with aniline, unlike those with $CHCl_3$ are not maximum for all compounds at the 1:1 ratio. For acetonitrile (N°3), methanol (N°13), and Et_2O (N°20) the plots of heat of mixing vs. composition are asymmetric and the maximum thermal effect is obtained at another ratio than 1:1. Hence, consideration of these points with other ones is invalid. The exclusion of three compounds from consideration raises the value of R to R=0.925; an additional exclusion of two compounds, dioxane (N°6) and anisole (N°1), gives the values R=0.956 and R=0.973, respectively. (a "satisfactory correlation"). For other 15 points the following equation was obtained:

$$\Delta H = -101.36 + 965.11 f(n) - 1354.37 f(\varepsilon) + 9514.18 \delta^2 - 1.201 B - 44.378 E$$

with R=0.973 and s=67.19 and with pair coefficients of correlation $r_{o1}=0.526$, $r_{o2}=0.545$; $r_{o3}=0.191$; $r_{o4}=0.650$; $r_{o5}=0.173$.

The signs on the regression coefficients indicate that the ability of compounds to the non-specific solvation, especially increase in their cohesion energy, increases

the value of heat of mixing with aniline and the ability to the specific solvation decreases it. To estimate the significance of some parameters we excluded them by turn and calculated the values of R each time [7]. The value of r decreases then to 0.970; 0.900; 0.941; 0.840, and 0.965 . Thus the parameters of polarizability and electrophility are relatively insignificant. This is confirmed by low values of pair correlation coefficients r_{oi} with these parameters. But with excluding both these parameters R de-

Table 1

HEATS OF MIXING OF ANILINE WITH ORGANIC SOLVENTS ΔH cal/mole (RATIO 1:1,25°) AND PARAMETERS OF SOLVENTS

N°	Solvent	ΔH	f(n)	f(ε)	δ^2	B	E
1	Anisole	+84.3	0.3030	0.384	0.097	255	1.4
2	Acetone	-285	0.2201	0.465	0.095	224	2.1
3	Acetonitrile(asymm.)	-59.8	0.2119	0.480	0.152	160	5.2
4	Benzene	+ 164	0.2947	0.231	0.085	48	2.1
5	Brombenzene	+230	0.3232	0.373	0.096	40	0
6	Dioxane	+355	0.2543	0.223	0.110	237	4.2
7	Dichloromethane	-19.5	0.2556	0.420	0.095	23	2.7
8	p-Xylene	+297	0.2920	0.229	0.077	68	(1)
9	Mesitylene	+385	0.2938	0.231	0.077	77	0.8
10	Methylacetate	-135	0.2218	0.395	0.091	170	(1.6)
11	Nitrobenzene	+130	0.3215	0.479	0.113	67	0
12	Pyridine	-400	0.2989	0.441	0.104	472	0
13	Methancl(asymm.)	+36	0.2034	0.478	0.201	218	14.9
14	Toluene	+238	0.2926	0.238	0.080	58	1.3
15	CCl_4	+280	0.2742	0.225	0.076	0	0
16	Formamide	+308	0.2675	0.494	0.400	270	14.5
17	Chlorobenzene	+223	0.3064	0.377	0.087	38	0
18	Chloroforme	+46	0.2563	0.359	0.088	14	3.3
19	Ethylacetate	-147	0.2275	0.384	0.082	181	1.6
20	Et_2O(asymm.)	-119	0.2167	0.345	0.057	280	0

Table 2

HEATS OF MIXING OF ACETONE WITH ORGANIC SOLVENTS ΔH cal/mole (RATIO I:I, 25°) AND PARAMETERS OF SOLVENTS

N°	Solvent	H	f(n)	f(ε)	δ^2	B	E
1	Aniline *	+84.3	0.3354	0.399	0.107	346	6.2
2	Acetonitrile (at 45°)	-25.9	0.2119	0.480	0.152	160	5.2
3	Benzene	+46.0	0.2947	0.231	0.085	38	2.1
4	Water * (asymm.)	-41.6	0.2057	0.494	0.592	156	21.8
5	n-Hexane	+387	0.2289	0.186	0.053	0	0
6	n-Heptane	+408	0.2358	0.191	0.060	0	0
7	Dimethylaniline(at20°C)	+30	0.3225	0.362	0.095	422	(0)
8	Dimethylformamide	+8.9	0.2584	0.488	0.198	291	2.6
9	Dichloromethane	-216	0.2556	0.420	0.095	23	2.7
10	Nitromethane(at 45°)	-38.2	0.2327	0.480	0.170	65	5.1
11	Propionitrile	-15	0.2237	0.474	0.105	162	3.2
12	CS_2	+336	0.3548	0.261	0.098	(0)	(0)
13	Butanol *	+327	0.3238	0.457	0.112	231	10.3
14	i-Propanol *	+391	0.2302	0.460	0.130	236	8.7
15	Methanol *	+160	0.2033	0.477	0.196	218	14.9
16	n-Propanol *	+410	0.2344	0.455	0.137	237	10.6
17	Ethanol *	+267	0.2214	0.469	0.158	235	11.6
18	Tetrahydrofurane	+41	0.2451	0.404	0.076	287	0
19	Toluene	+52	0.2926	0.238	0.080	58	1.3
20	CCl_4	+45.2	0.2742	0.225	0.076	0	0
21	Formamide * (asymm.)	+90	0.2675	0.494	0.400	270	14.5
22	$CHCl_3$ (asymm.)	-454	0.2563	0.359	0.088	14	3.3
23	Cyclohexane (at 20°)	+397	0.2563	0.203	0.068	0	0
24	Ethylacetate	+31.7	0.2275	0.384	0.082	181	1.6
25	Ethylenglycole *	-212	0.2592	0.483	0.318	224	15.0
26	Diethyl ether	+120	0.2167	0.345	0.057	280	0

* Associated solvents

creased to R=0.915 i.e. is in the range of "poor correlation".

Thus the experimental values of heats of mixing of aniline with other substances are the total effect of specific and non-specific interactions among which the cohesion energy density δ^2(i.e. Van-der-Vaals interaction) and basicity exert the major influence and decrease the value of thermal effect. However, the total heat effect may be satisfactorily described by the five-parameter equation only which includes various kinds of interaction.

More complicated process is observed in the case of heats of mixing with acetone (Table 2). Here both the compounds which give the asymmetric curves of mixing (N°N° 4.21.25) and numerous associated compounds, mainly alcohols, are listed. In the Table they are marked by an asterisk. The total correlation coefficient R=0.572 is very low. When excluding the values for associated compounds and the compounds which give the asymmetric curves, the value of R grows up to 0.828. After an additional exclusion of the data for CCl_4(N°20) and CH_2Cl_2 (N°9) the satisfactory correlation with R=0.941 was obtained. For the remained 15 points we obtained the equation:

$$\Delta H = 568.97 - 1154.85f(n) - 232.39f(\delta) + 1940.34\delta^2 - 0.816\ B - 95.30\ E$$

with R=0.941; s=74.14 and pair coefficients of correlation $r_{01}=0.150$; $r_{02}=0.806$; $r_{03}=0.576$; $r_{04}=0.603$; $r_{05}=0.662$. Thus, as in the previous case, the thermal effect of mixing depends on the various aspects of compound interactions. Due to a low value of the total correlation coefficient R we do not determine the significance of separate parameters by their exclusion, but the values of both pair correlation coefficients and regression coefficients show that the cohesion energy density of the second component exerts the most influence on the value of heat of mixing.

In this way the thermodynamic effects of mixing of one compound with a series of other compounds may be satisfactorily calculated by the linear free energy multiparameter equation on the basis of their properties. This equation was proposed for determining solvent effects on kinetic and spectral phenomena[8]. But in this case it should be supplemented by the parameter calculating the energy density $\delta^2 = \frac{\Delta H - RT}{V}$. Necessary conditions are that the maximum (minimum) thermal effect should be observed at the 1:1 ratio and the second component should not be associated. In the first place the hydrogen bond should be absent. The calculation results are better, when the magnitudes of thermal effects are larger. This may be accounted for by the appearance of great experimental errors in the case of low values of heats of mixing.

L I T E R A T U R E

1. I.A. Koppel and A.I. Paju, Reakts.sposobn.organitsh. soed. II, 121 (1974).
2. R.G. Makitra, Ya.N.Pirig, R.V. Sendega, and O.E. Turkevich DAN Ukr. SSR, ser."B", 1976, 998.
3. V.G. Tsvetkov, B.I. Kosyrkin, L.Ya. Tsvetkova, and I.B. Rabinovich, Zh.obsh.khim. 48,2162 (1978)
4. V.P. Belousov and A.G. Moratshevskij, Heats of Mixing of Liquids, "Khimiya", Leningr. 1970. (In Rus.).
5. I.A. Koppel and A.I. Paju, Reakts. sposobn.organitsh. soed. II, 139 (1974).
6. V.A. Palm, Fundamentals of Quantitative Theory of Organic Reactions. "Khimiya", Leningr. 1977, p.315.
7. N.B. Chapman, M.R.J. Dack, D.J. Newman, J.Shorter, and R. Wilkinson, J.Chem.Soc., 1974, Perkin Trans. p.2, 963.
8. I.A. Koppel and V.A. Palm in "Advances in Linear Free Energy Relationships", Plenum Press, London, 1971.

KINETICS AND MECHANISM OF THE ELIMINATION OF α- AND β-SUBSTITUTED β-PIPERIDINOPROPIONITRILES

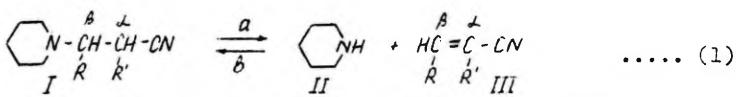
O.Adoménienė and G.Dienys

V.Kapsukas State University, Vilnius, Lithuanian S.S.R.

Received April 10, 1979

The reactions of the elimination of α- and β-substituted β-piperidinopropionitriles were studied conductometrically in water and water-dioxane solutions. Elimination proceeds via the attack of hydroxyl ion on the protonated form of β-piperidinopropionitriles. All the substituents studied promote the elimination, except α-methyl, resulting in a slight rate decrease. α-Phenyl substituent accelerates the reaction by 3 orders. The primary deuterium isotope effect of β-methyl-β-piperidinopropionitrile, k_H/k_D, is 5.2 in H_2O and 5.0 in D_2O.

Kinetics of addition of aliphatic amines to acrylonitrile and its derivatives has been fairly thoroughly investigated by us [1-3], the reversibility of these reactions was discussed [3]. In the present paper we report our studies on kinetics and mechanism of the elimination of α- and β-substituted-β-piperidinopropionitriles (reaction 1a):

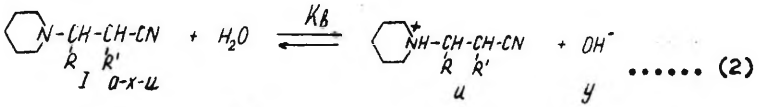


..... (1)

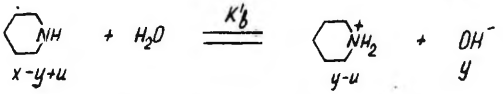
R, R' = H, H (a); H, CH_3 (b); H, C_6H_5 (c); CH_3, H (d); C_2H_5, H (e); $CH(CH_3)_2$, H (f); C_6H_5, H (g).

As a result of the basic dissociation of amines (reactions 2 and 3), two forms of β-piperidinopropionitriles (amine I, protonated amine IV) and four nucleophiles (hydroxyl ions, piperidine, adduct I, water) are present in the

reaction mixture:

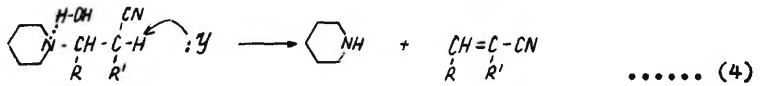


..... (2)

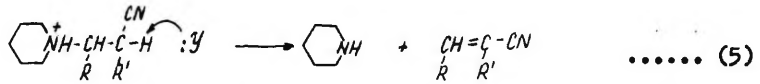


..... (3)

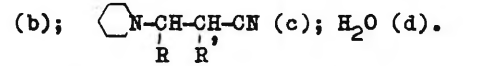
a is initial concentration of I; x,y,and u are concentrations of elimination product III, hydroxyl ions, and protonated amine IV. Therefore eight parallel reactions of the bimolecular elimination E2 are possible:



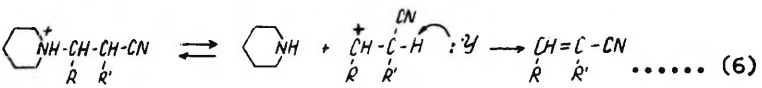
..... (4)



..... (5)

Y: = OH^- (a);  (b);  (c); H_2O (d).

Unimolecular elimination E1 of compounds IV (reaction 6) and nucleophilic substitution (S_N2) of piperidine by hydroxyl ions are possible, too.



..... (6)

Relative contributions of various mechanisms to experimentally determined rate of the elimination would vary in the broad limits with the course of the reaction, as the relative concentrations of different particles in the reaction mixture change substantially. The same would happen if the pH of the reaction mixture is changed by adding an acid or a base. By means of gas chromatography we have shown, that the elimination reaction does not take place,

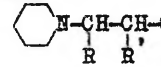
if compound Id is dissolved in 2M HCl or 2M NaOH, i.e. under the conditions, particularly favourable for reactions (5d), (6) and (4a). It means that the rate of the elimination reaction via mechanisms (4a), (5d) and (6) is negligible (by quantitative evaluation - less than 0.01%) as compared with the experimental rate of the elimination reactions in the water solution, without addition of an acid or a base. Reactions (4b-d) may be neglected too, as they are analogous to (4a), but with less active nucleophiles. The product of nucleophilic substitution, β-oxy-β-methylpropionitrile, was not found in the reaction mixture.

We have written a program for digital computer, which enabled calculation of any set of the rate constants of reactions (1b, 4-6) and of relative contributions of reactions (4-6) to the experimentally observed rate of elimination. These calculations showed that all the reactions except (5a) do not take an appreciable part in the elimination process. Thus it was shown, that equilibrium (1) in the case of compound Id involves only two reactions - the addition reaction (1b) and the elimination reaction (5a). We suppose that it works also for other β-piperidinopropionitriles, as the rates of the elimination reactions for these compounds differ from each other not very much.

In order to get information about a type of the transition state of the elimination [4] we have studied an influence of alkyl- or phenyl-substitution and of α-deuteration on the rate of reaction (1a).

The influence of substituents was studied in water and water - dioxane solutions (Table 1). The reason for using mixed solvent was the limited solubility in water of several of compounds I. A drawback of this solvent is a possibility of systematic deviations in the values of basic dissociation constants of amines I, and, hence, in the values of the rate constants of the elimination reactions.

Table 1

Rate Constants of Reaction (5a) ($l \cdot mol^{-1} \cdot s^{-1}$) and the Values of Acid Dissociation Constants (pK_a) of Compounds  (I) at 45°C.

The compound	R	R'	k, in water	$k \cdot 10^{-3}$, in 40% dioxane	pK_a in water	pK_a in 40% dioxane
Ia	H	H	3.40±0.08	*0.97±0.03	7.26±0.03	6.57±0.03
Ib	H	CH_3	1.28±0.07	0.46±0.03	7.19±0.02	6.44±0.04
Ic	H	C_6H_5	-	1080±20	-	5.50±0.03
Id	CH_3	H	76 ± 2	2.98±0.04	7.31±0.03	6.70±0.04
Ie	C_2H_5	H	146 ± 4	4.24±0.07	7.23±0.03	6.57±0.05
If	$CH(CH_3)_2$	H	-	5.54±0.08	-	6.12±0.02
Ig	C_6H_5	H	-	13.2±0.2	-	5.48±0.05

* standard deviations of 4 - 5 parallel experiments are given.

Nevertheless, the rate constants obtained do give information on the influence of substituents and of a solvent on the rate of elimination. The results are consistent with a bimolecular elimination mechanism E2, including a carbanionic character of the transition state (ElcB-like mechanism). This conclusion is supported by the value of kinetic isotope effect. The rate constants of elimination of compound Id and it's α-deuterated analogue in H_2O and D_2O solutions are presented in Table 2. The isotope effect is rather high and is close to the values given in the literature for the reactions believed to be on the borderline between concerted and stepwise (ElcB) processes[5-7].

Table 2

Rate Constants of β-Methyl-β-Piperidinopropionitrile and α-D_2-β-Methyl-β-Piperidinopropionitrile Elimination Reactions (k_H and k_D, respectively, $l \cdot mol^{-1} \cdot s^{-1}$) in H_2O and D_2O at 45°C.

Solvent	k_H	k_D	k_H/k_D
H_2O	76± 2	14.5± 0.4	5.2
D_2O	320± 6	64 ± 2	5.0

The rate constants of reaction (1b) (nucleophilic addition of piperidine to substituted acrylonitriles) were calculated from experimental data of elimination processes along with the rate constants of reactions (4 - 6). The accuracy of such calculations was checked by determining the rate constants of reaction (1b) from the initial rate of the addition reaction in independent experiments (Table 3). The values of the rate constants found in both ways were in close agreement.

Table 3

Rate Constants of the Addition of Piperidine to β-Substituted Acrylonitriles ($l \cdot mol^{-1} \cdot s^{-1}$, 45°C).

R in R-CH=CH-CN	$k \cdot 10^2$	
	in water [*]	in 40% dioxane
H	223± 3	10.6± 0.4
cis-CH_3	5.21±0.09	1.32± 0.08
trans-CH_3	4.61±0.05	1.02± 0.09
cis-C_2H_5	2.32±0.07	0.74± 0.06
trans-C_2H_5	0.95±0.05	0.32± 0.04

[*] from Ref. [3].

The increase in the elimination rate constants by three powers of ten (Table 1), as well as some decrease in the addition reaction rate (1b) with decrease in the solvent polarity (Table 3) are consistent with the literature data on the influence of solvent upon the rate of analogous reactions [8,9].

Experimental

Materials.

α-Methylacrylonitrile was synthesized by acetylation of acetone cyanohydrin followed by pyrolysis of acetone cyanohydrin acetate [11,12]. α-Phenylacrylonitrile was synthesized according to [13], the synthesis of β-substituted acrylonitriles was described in [3], α- and β-substituted β-piperidinopropionitriles were obtained by refluxing appropriate α- or β-substituted acrylonitriles with excess of piperidine, containing catalytic amounts of water (compound Ic was obtained at room temperature). Compounds Ia, Ib, Id, and Ie were purified by two-fold vacuum distillation, compound Ie was additionally purified by chromatography on alumina. The R, R', and b.p.°C/mm are given: H, H, 85/4; H, CH_3, 72/2; CH_3, H, 96/4; C_2H_5, H, 108/4; $(CH_3)_2CH$, H, 119/4. Compounds Ic and Ig were purified by chromatography followed by crystallization from hexane, m.p.47°C and 55°C. The purity of compounds I was controlled by thin layer chromatography, their structure was confirmed by the data of elementary analysis and PMR spectroscopy. β-Oxy-β-methylpropionitrile was synthesized by the reaction of trans-crotononitrile with an excess of aqueous alkali (70°C, 30 hours) followed by an extraction of the acidified reaction mixture, evaporation of the solvent and distillation of the product through Vigreaux column (b.p.220-222°C, 23% yield). α-D_2-β-methyl-β-piperidinopropionitrile (Ih) was obtained in a following way: 0.03 mol(4.6 g) β-methyl-β-piperidinopropionitrile and 0.02 mol(1.7 g) piperidine-1-D were refluxed for 8 hours with the mixture of D_2O - dioxane (60:40), the solvent and piperidine were evaporated, the residue was distilled upon vacuum through a 10 cm Vigreaux column. The procedure described was repeated three times; b.p. 96-98°C/4mm, 52% yield. The degree of deuteration was controlled by means of PMR-spectroscopy (by comparing the integral intensity of proton signals) and by means of mass-spectroscopy. According to the data of both

methods, 92% of protons in α-position of β-methyl-β-piperidinopropionitrile was substituted by deuterium. Besides, according to the data of mass spectrometry 13% of protons in β-methyl group of compound Ih were substituted by deuterium. Piperidine-1-D was obtained according to [14], dioxane was purified according to [15].

pK_a - Determination.

The pK_a - values of compounds Ia, Ib, Id and Ie in aqueous solution were determined by potentiometric titration in usual way [16]. 0.01 M solutions of compounds Ia-Ig and piperidine in 40% dioxane were titrated potentiometrically with 0.1 M HCl solution. pH-meter was calibrated by using standard buffer solutions in water. pK_a of piperidine equals 9.90 ± 0.03 in 40% dioxane at 45°. Values of pK_a of compounds Ia-Ig are given in Table 1. The value $pK_w = 14.834$ [17] (40% dioxane, 45°) was used for calculation of pK_b. pK_a of compounds Id and piperidine-1-D in heavy water was determined potentiometrically by titration with 0.1 M DCl solution; a correction for glass electrode was made ($pD = pH_{measured} - 0.41$ [18]). The pK_a values are 11.07 for piperidine and 7.82 for compound Id at 45°. The value $pK_w = 14.241$ [19] was used for the calculation of pK_b values.

Chromatographic analysis of β-methyl-β- piperidinopropionitrile elimination products.

a) 0.15 g of compound Id was dissolved in 50 cc water, kept at 45° during 5 hours. The reaction mixture was acidified with HCl and extracted with diethyl ether (5 x 20 cc). The solvent was evaporated on a water bath through Vigre column (height 20 cm), the column was washed by 0.3 cc diethyl ether, the solution obtained (ca. 0.5 cc) was analyzed by means of gas chromatography. Both trans- and cis-β-methylacrylonitriles IIId were found in the solution in a ratio 1.1:1.0, the total amount corresponds to 36% of initial compound Id. β-Oxy-β-methylpropionitrile (V) was absent.

b) 0.15 g of compound Id was dissolved in 50 cc 2 M HCl, then the solution was treated as in "a". Compounds IIId

and V were absent in the extract.

c)0.15 g of compound Id was dissolved in 50 cc of 2M NaOH. After treating the solution obtained as described in "a", compounds IIId and V were not found in the extract.

The kinetics of the elimination of α- and β-substituted β-piperidinopropionitriles.

0.005-0.02 M solutions of compounds I were prepared by dissolving an appropriate amount of I in a conductometric cell, containing 20 cc solvent. Kinetics of reaction (1) was studied conductometrically in water and water-dioxane (5:4 by weight) solutions. The technique of obtaining the rate values during the reaction course was described elsewhere. The concentrations of hydroxyl ions and those of protonated amines were calculated from the equations:

$$K_b = u \cdot y/(a-x-u) \; ; \quad K_b' = (y-u) \cdot y/(x-y+u) \qquad \ldots\ldots (7)$$

The rate constants of reaction (5a) were calculated from the equation:

$$k_i = \left[(dx/dt)_i + k_{1b} \cdot x_i (x_i - y_i + u_i)\right] / u_i \cdot y_i \qquad \ldots\ldots (8),$$

where $(dx/dt)_i$ is a value of the reaction rate at the time t_i (50 - 70% of reaction depth was used for calculation), k_{1b} is an experimental value of addition reaction (1b) rate constant, x_i, y_i, and u_i are concentrations of piperidine, hydroxyl ions, and compound IV. The reaction rate constant k was calculated as an arithmetic mean of 30 - 50 k_i values.

The rate of the addition reaction is negligible as compared with the rate of elimination reaction in the case of compounds Ib, If, Ig (the values of addition reaction rate constants in water solutions are given in [1,3]), therefore the elimination rate constants were calculated from equation $k_i = (dx/dt)_i / u_i \cdot y_i$. The rate constant of the elimination of compound Ic was found from the initial rate of the reaction, because of the rapid dimerization of

α-phenylacrylonitrile IIIc [20]. All the calculations were performed on the digital computer "Minsk-22".

The kinetic isotope effect.

The kinetics of elimination reactions of compound Id and α-D_2-β-methyl-β-piperidinopropionitrile (If) was studied in H_2O and D_2O solutions at 45°C conductometrically. The rate constants of reaction (5a) for isotopically different substrate and solvent were calculated from the initial rate values. In the case of isotopically identical substrate and solvent the rate constants were calculated from equation (8) as well as from the initial rate values; both methods gave the same values. The values of rate constants were corrected for an admixture of undeuterated compound Id.

References

1. G.Dienys, L.Arkhipova, R.Pupenytė, M.Danilevičiūtė, and L.J.Kunskaitė, Reakts. sposobn. organ. soedin. 9, 345 (1972).
2. G.J.Dienys, L.J.J.Kunskaitė, A.K.Vaitkevičius, and A.V.Klimavičius, Organic Reactivity, 12, 275 (1975).
3. O.Adoménienė, G.Dienys, and Z.Stumbrevičiūtė, Organic Reactivity, 15, 38 (1978).
4. D.V.Banthorpe, Elimination Reactions, Elsevier, Amsterdam-London-New York, 1963, p.16.
5. R.A.More O Ferrall, in Structure and Dynamics in Chemistry, Proceedings from Symposium held at Uppsala, Uppsala, 1978, p. 209.
6. V.Fiandanese, G.Marchese, and F.Naso, J.Chem.Soc.,Perkin Trans.,II, 1973, 1538.
7. R.A.More O'Ferrall and S.Slae, J.Chem.Soc.(B),1970,260.
8. C.K.Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca and London, 1969.
9. K.A.Cooper, M.L.Dhar, E.Hughes, C.K.Ingold, B.J.MacMulty, and L.J.Woolf, J.Chem.Soc.,1948, 2040.

10. A.Y.Yakubovitch, J.Appl.Chem.(Rus.)21, 151 (1948).
11. W.J.Bailey, F.E.Naylor, and J.J.Hewitt, J.Org.Chem., 22, 1067 (1957).
12. R.Burns, D.Trevor Jones, and P.D.Ritchie, J.Chem.Soc., 1935, 400.
13. W.C.Davies and W.J.Jones, J.Chem.Soc., 1929, 33
14. A.Murray, III, and D.L.Williams, Organic Syntheses with Isotopes, part II, Compounds of Isotopic Hydrogen, Interscience Publishers, New York, London, 1958.
15. A.J.Gordon and R.A.Ford, The Chemist's Companion,A Wiley-Interscience Publication, New York-London-Sydney-Toronto, 1972.
16. A.Albert and E.P.Serjeant, Ionisation Constants of Acids and Bases, Methuen and Co., London, 1962.
17. H.S.Harned and B.B.Owen, Physical Chemistry of Electrolytic Solutions, Reinhold Publishing Corp., N.Y., 1950.
18. K.Mikkelson and S.O.Nielsen, J.Phys.Chem.,64, 632 (1960)
19. A.K.Covington, R.A.Robinson, and R.G.Bates, J.Phys.Chem., 70, 3820 (1966).
20. J.M.Stewart and Ch.H.Chang, J.Org.Chem., 21, 635 (1956).

STRUCTURAL EFFECTS ON pK_{R^+} OF ARYLMETHANOLS AND POLYLINEARITY EQUATIONS

B.I.Istomin

Petroleum Synthesis Institute at Irkutsk University, P.O. Box 1665, Irkutsk 664033 U.S.S.R.

Received April 15, 1979

The multiple regression analysis of the literature data reveals that the values of pK_{R^+} of an equilibrium (I) for arylmethanols follow adequately non-additive polylinear Eqns.(20) and (4),when a structural effect measure X evaluated by Eq.(3) or constants σ^+ are used.The results are discussed.

Numerous investigations in the last years show unambiguously significant non-additivities in the effects of the factors affecting the reactivity and physico-chemical properties of organic compounds. However,it is often difficult to estimate accurately an extent of actual non-additivity in the effects of factors considered. The reasons of those difficulties are usually the following[1]. Since various substituent constants or solvent parameters are usually used as the independent variables in the modelling polylinear expansions it is often impossible to reduce the non-orthoganalities between those variables themselves as well as between them and their products. That may lead to biasing estimates of the modelling equation coefficients. With no theoretical values for all those coefficients or for part of them one has usually no way to control the account of these biasings. As a result, one can find for any process or a property several multiple regressions which have different formal or/and physical meanings[2,3+] being statistically equivalent at the same time. A choice of an actual one from these regressions may be quite a difficult problem.For example, the following situation is often observed[1]. The mul-

+The regressions with different cross-terms, for example.

tiple regression analyses of the experimental data for a reaction series might give three statistically equivalent equations, when one of the factors used is temperature and the other ones are usual structural and/or solvent parameters. One of those regressions pretends that an activation energy in the series should be quite independent of the structural and/or solvent factors, i.e. the series is isoenthalpic, whereas the another regression represents the same series as an isoentropic one. The third regression shows at the same time that the compensation law[2] should be observed in that series.

In order to overcome these difficulties it has been proposed[4-6] to make use of "inner" ("intrinsic") scales (measures) for the effects of the factors affecting the property of interest. Using such scales one has the theoretical values[2,3] for all coefficients at the additive terms of the multiple polylinear equations. These values enable to control biasings in the estimates for those coefficients. The method has been used successfully to reveal non-additivities in the effects of X_I and X_2 on alkaline hydrolysis[4] of $X_IX_2P(O)F$, on chemical shifts[5] $I3^2_C$ for para-disubstituted benzenes[5] XC_6H_4Y as well as non-additivity in structural and solvent effects on proton transfer equilibria[6]. In order to check the method once more it is used here for analysis of structural effects on equilibrium constants K ($-\log K = pK_R+$) for the formation (I) of carbonium ions from m,p-substituted triaryl- and diarylmethanols[7] in aqueous acids at 25°

$$R_IR_2R_3COH + H^+ \overset{K}{\rightleftharpoons} R_IR_2R_3C^+ + H_2O \qquad (I)$$

R_I and R_2 are aryls, and R_3 is an aryl or H. The experimental data for this process are listed in Table I. Three main reasons force us to make this choice:

1°. For this process there are many experimental data, e.g. see Refs. 7-9, and the values of pK_R+ vary widely with structural variations (see Table I).

2°. The structural effects on the free energy change in this process are shown[9] to be non-additive to a large extent;

Table I

Experimental pK_R^+ - Values[7-9] for the Carbonium Ion Formation Equilibria (I) from m,p-Substituted Arylmethanols in Aqueous Acids at 25° [a]

No.	Compound	pK_R^+	No.	Compound	pK_R^+
I	$(p\text{-HO}\phi)_3\text{COH}$	I.97	25	$(p\text{-Me}_2\text{N}\phi)_2\text{COH}$ p-MeOφ	7.I8
2	$(p\text{-MeO}\phi)_3\text{COH}$	0.82			
3	$(p\text{-MeO}\phi)_2\text{PhCOH}$	-I.I3∓0.I5	26	$(p\text{-NMe}_2\phi)_3\text{COH}$	9.36
4	$(p\text{-MeO}\phi)\text{Ph}_2\text{COH}$	-3.40∓0.I6	27	$(p\text{-NMe}_2\phi)_2$ m-ClφCOH	6.23
5	$(p\text{-Me}\phi)_3\text{COH}$	-3.56			
6	$(p\text{-Me}\phi)_2\text{PhCOH}$	-4.7I	28	$(p\text{-NMe}_2\phi)_2$ m-MeφCOH	7.21
7	$(p\text{-Me}\phi)\text{Ph}_2\text{COH}$	-5.39∓0.20			
8	$(m\text{-Me}\phi)_3\text{COH}$	-6.I5∓0.28	29	$(p\text{-NMe}_2\phi)_2$ p-MeφCOH	7.27
9	$(p\text{-Bu}\phi)\text{Ph}_2\text{COH}$ [b]	-6.I			
I0	$(p\text{-Bu}\phi)_2\text{PhCOH}$ [b]	-6.6	30	$(p\text{-NH}_2\phi)_3\text{COH}$	7.57
II	$(p\text{-Bu}\phi)_3\text{COH}$ [b]	-6.5	31	$(p\text{-NH}_2\phi)_2\text{PhCOH}$	5.38
I2	$(p\text{-Pr}\phi)_3\text{COH}$ [c]	-6.54	32	$(p\text{-NMe}_2\phi)\text{Ph}_2\text{COH}$	4.75
I3	Ph_3COH	-6.64∓0.I9	33	$(p\text{-NH}_2\phi)\text{Ph}_2\text{COH}$	4.6
I4	$(p\text{-F}\phi)_3\text{COH}$	-6.05	34	$(p\text{-MeO}\phi)_2\text{HCOH}$	-5.66∓0.(
I5	$(p\text{-Cl}\phi)_3\text{COH}$	-7.83∓0.I6	35	$(p\text{-Me}\phi)_2\text{HCOH}$	-I0.4
I6	$(p\text{-NO}_2\phi)\text{Ph}_2\text{COH}$	-9.45∓0.3I	36	$(p\text{-F}\phi)_2\text{HCOH}$	-I3.03
I7	$(p\text{-NO}_2\phi)_2\text{PhCOH}$	-I3.I8∓0.39	37	$(p\text{-Bu}\phi)_2\text{HCOH}$ [b]	-I3.2
I8	$(p\text{-NO}_2\phi)_3\text{COH}$	-I7.I8∓0.92	38	Ph_2HCOH	-I3.3
I9	$(p\text{-NMe}_2\phi)\text{Ph}_2$ HOC	7.0I∓0.I5	39	$(p\text{-Cl}\phi)_2\text{HCOH}$	-I3.96
			40	$(p\text{-Br}\phi)_2\text{HCOH}$	-I4.I6
20	$(p\text{-Me}_2\text{N}\phi)_2$ m-$_2$ONφCOH	5.84	4I	$(p\text{-J}\phi)_2\text{HCOH}$	-I4.26
			42	$(p\text{-NMe}_2\phi)_2\text{HCOH}$	5.6I
2I	$(p\text{-Me}_2\text{N}\phi)_2$ p-$\text{NO}_2\phi$COH	5.50	43	$(p\text{-MeO}\phi)\text{PhHCOH}$	-7.9
			44	$(p\text{-Me}\phi)\text{PhHCOH}$	-II.6
22	$(p\text{-Me}_2\text{N}\phi)_2$ m-BrφCOH	6.23	45	$(p\text{-Et}\phi)\text{PhHCOH}$	-II.6
			46	$(p\text{-Pr}\phi)\text{PhHCOH}$ [c]	-II.6
23	$(p\text{-Me}_2\text{N}\phi)_2$ p-BrφCOH	6.38	47	$(p\text{-Bu}\phi)\text{PhHCOH}$ [b]	-II.8
24	$(p\text{-Me}_2\text{N}\phi)_2$ m-MeOφCOH	7.08			

[a]The data are from the compilation in Ref.7 or from Refs. 8 and 9. If in these sources there are several pK_R^+ -values varied within I log.unit for the same compound we use here their arithmetic means. The standard deviations are listed in Table I for such values. [b] Bu is substituent t-Bu. [c]Pr is i-Pr.

3° However, all the known data for equilibrium (I) are not described adequately within the generalized equation up to now.[10] The correlation of pK_R^+ with σ^+ constants for the compounds with two unchangeable substituents were described[8,9], but their statistics are unsatisfactory; poor correlation coefficients and large regression standards are observed. Somewhat better results were found[10,11] within the dual equation of Yukawa and Tsuno.

Let us assume now that substituents R_1, R_2 and R_3 have actually non-additive effect on the free energy changes in equilibrium (I). The corresponding pK_R^+'s should follow[2,3] thereon the equation

$$pK_R^+(R_1,R_2,R_3) = a_0 + a_1\sum_i X_i + a_2\sum_i\sum_j X_i X_j + a_3\prod_i X_i \qquad (2)$$

when one defines[2,3] the measure X for the substituent effect on this process as the difference

$$X_i = pK_R^+(R_i,R_0,R_0) - pK_R^+(R_0,R_0,R_0) \qquad (3)$$

taking arbitrary any aryl group as a standard substituent R_0. X is an "intrinsic" scale[4-6]. Then the coefficients a_0 and a_1 in Equation (2) should be[2,3] equal to $pK_R^+(R_0,R_0,R_0)$ and 1.00, respectively, whereas the coefficients a_2 and a_3 are considered to characterize[2,12] the intensities of double and triple interactions between the substituents. Taking successively the groups Ph and $Me_2N\emptyset$ as a standard substituent R_0, we evaluate two scales X_A and X_B for various groups R (see Table 2). Table 3 contains the results (Regs. A-F) obtained by the multiple regression analyses, in the framework of Eq.(2) and with scales X_A and X_B, of the pK_R^+ values for tri and diarylcarbi-

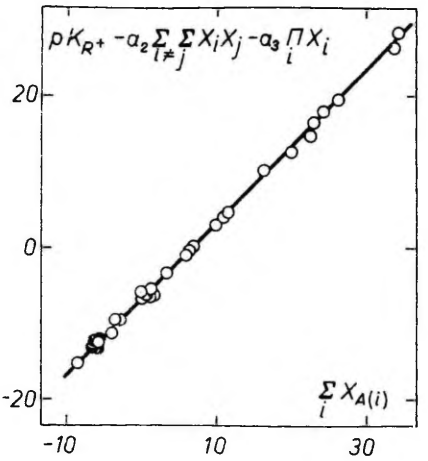


Fig.I. Illustration of Eq.(2) in the form of Reg.A of Table 3 for equilibrium (I). Close and open points correspond to di- and triarylmethanols, respectively.

Table 2

Parameters X for Various Substituents

Substituent	X_A^a	X_B^b	Substituent	X_A^a	X_B^b
p-MeOØ	3.24	-2.I8	m-NO_2Ø		-3.52
p-MeØ	I.25	-2.09	m-BrØ		-3.I3
p-(t-Bu)Ø	0.54		p-BrØ		-2.98
p-NO_2Ø	-2.8I	-3.86	m-MeOØ		-2.28
p-NMe_2Ø	II.39	0.00[c]	m-ClØ		-3.I3
p-NH_2Ø	II.24		m-Me		-2.I5
Ph	0.00[c]	-2.35	H	-6.66	

[a]These values are evaluated according to Equation (3), when R_0 = Ph. [b]These values are derived from Equation (3), taking group p-Me_2NØ as R_0. [c]In accordance with the definition; see Equation (3).

nols. Taking into account the results of Refs.8,9, one may assume that relationship(4) similar to Eq.(3) should also

Table 3

Coefficients and Statistics for Equations (2) and (4)

Reg.	Variable	a_0	a_I	a_2	a_3	n	R	S_0	Signif. deviated points[a]
A[b]	X_A	-6.937±0.102	1.008±0.025	-0.074±0.005	0.0068±0.0008	22	0.9976	0.56	---
B[b]	X_A	-7.102±0.220	0.879±0.043	-0.040±0.005	---	22	0.9876	1.24	---
C[b]	X_A	-6.651±0.461	0.556±0.046	---	---	22	0.9373	2.67	---
D[b]	X_A	-6.912±0.066	1.002±0.023	-0.073±0.004	0.0064±0.0007	30	0.9973	0.60	---
E[d]	X_A	-8.497±0.227	0.736±0.050	-0.100±0.034	---	8	0.9937	0.84	---
F[b]	X_B[f]	9.367±0.463	1.011±0.178	-0.681±0.082	-0.284±0.048	21	0.9979	0.58	2,3
G[b]	σ^+[e]	-7.053±0.136	-4.144±0.102	-0.062±0.142	0.960±0.167	28	0.9971	0.59	10-12,32,33
Ga[b]	σ^+[e]	-7.058±0.095	-4.131±0.057	---	1.010±0.081	28	0.9978	0.52	10-12,32,33
H[d]	σ^+[e]	-13.112±0.049	-4.130±0.242	1.756±0.307	---	12	0.9990	0.27	37,43
I[c]	σ^+[e]	-6.641±0.048	-3.960±0.057	---	1.031±0.089	41	0.9961	0.76	10-12,32,33, 43

[a]The significantly deviated points are numerated in accordance with the numeration in Table I. [b]For triarylcarbinols. [c]For di- and triarylcarbinols. [d]Only for diarylmethanols. [e]Constants σ^+ are from Ref.10. [f]Parameters X_B for p-ClØ, p-IØ and p-FØ are assumed to be as large as that one for p-BrØ.

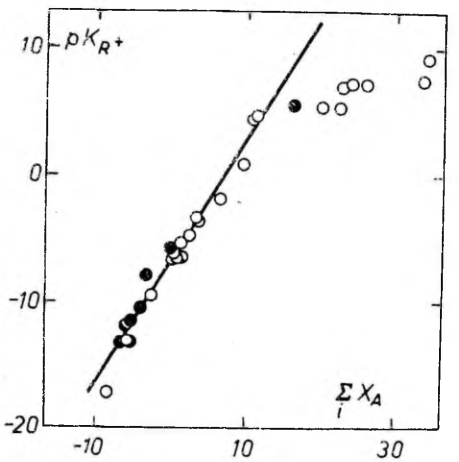


Fig. 2. The plot of pK_{R^+} vs the additive term $\sum_I X_{A(i)}$ of Equation (2).

$$pK_{R^+}(R_1,R_2,R_3) = a_0 + a_I\sum_i \sigma_i^+ + a_2 \sum_i\sum_j \sigma_i^+\sigma_j^+ + a_3\prod_i \sigma_i^+ \qquad (4)$$

exist. In Table 3, Regs. G-I correspond to the last equation.

On the basis of Table 3 one can draw the following conclusions:

I. Being based on the scale X_A, Equation (2) describes adequately[+] (Reg. A, Fig. I) pK_{R^+}'s for 22 triarylcarbinols. The variation in the property correlated is as large as 26.5 in log. units from $(p\text{-}NO_2\text{Ø})_3COH$ to $(p\text{-}Me_2N\text{Ø})_3COH$; see Table I. As to the other triarylmethanols of Table I, the measure X_A is unknown for one of their three substituents, at any rate. In Reg.A, the estimate for a_0 within the regression standard as well as the estimate for a_I within its uncertainty are in good agreement with the corresponding theoretical values[2,3,12].

[+]Ref. 8b estimates a real accuracy of the pK_{R^+}-values measured as ±0.05 in log. units.

Coefficients a_2 and a_3 are highly significant. Comparing Figs I and 2, one sees the actual role of non-additive terms in pK_R^+ values considered. Reg. A is related to differences of the corresponding contributions in the free energies of the ions and the parent alcohols. Hence, two extremes are possible theoretically. That is, significant contributions of interactions between the substituents which are described by the non-additive terms in Equation (2) are only in the free energy of the carbinols or in the free energy of the corresponding ions. It is impossible to make choice between these alternatives within the present results only. We believe, however, that the free energies of these both species are non-additive to a large extent+. When the terms related to double and triple interactions between the substituents are excluded from Eq.(2)(see Reg.B and C), its accuracy grows worse drastically and the coefficients a_I are in large bias as well. These facts prove once more that the "inner" scales for factors are very useful to reveal the actual character in combined effect of several factors on organic reactivities.

2. pK_R^+'s for diarylcarbinols also fit (see Reg. E) Equation (2), when the measures X_A are used for their aryl groups. Having defined X_A for substituent H by Equation (3), one finds that the values of pK_R^+ for di - and triarylcarbinols are accurately described by the same regression (see Reg. D and Fig.I). All its coefficients and statistics do not differ from those found for triarylcarbinols (Reg. A). Hence, it is reasonable to assume that di- and triarylmethanols form the same reaction series. The substituent H, in accordance with its measure X_A, is more powerful destabilizer of a cation or more powerful stabilizer of the parent alcohol than group p-$NO_2\emptyset$

+The formation enthalpies ΔH_f^o of polysubstituted alkanes as well as of alkanes themselves are highly non-additive[12] and are found to be described accurately by the polylinear equation similar to Eq.(2). Non-additivities are also found in the formation enthalpies of aliphatic carbonium ions.

(See Table 2). The differences observed between the coefficients a_0 + a_2 in Regs. D (or A) and E arise from Equation (2).

3. The scale X_B also leads to the adequate representation (See Reg.F) of pK_R+'s for Ar_3COH. The estimates found for a_0 and a_I agree well with their theoretical values; both coefficiants a_2 and a_3 are significant statistically. According to V. Palm[2], the coefficients a_2 and a_3 in polylinear equations similar to (2) should obey the following conditions: $a_2 = \alpha$ and $a_3 = \alpha^2$, when the "inner" scales are used for the factors considered. Within their uncertainties, the corresponding estimates in Regs. A and D obey those requirements. However, a replacement of the "zero point"[I2] for expansion, i.e. replacement of the standard substituent R_0 leads, in spite of Ref. 2 to disappearence of these ratios (See Reg. F, $a_2 < 0$ and $a_3 < 0$). Hence, these conditions[2] are not universal[+].

4. Equation (4) is found to describe (See Regs.G and Ga) the values of pK_R+ for Ar_3COH, when some significantly deviated points are excluded. However, the double interaction term is insignificant, in spite of the results of Ritchie[8]. Good statistics of these regressions are rather surprising because the pK_R+ values of various special cases of series (I), when one aryl substituent is varied, show only satisfactory correlations vs constants σ^+. Having used Reg.Ga, one can calculate formaly the constants σ^+ for substituent H: σ^+=I.80. The close estimate (I.74) may be derived as well from the ratio of a_2 and a_3 in Regs. H and Ga. That value allows to describe all tri and diarylcarbinols of Table I with good accuracy within the same regression (Reg.I).

5. Since Regs. A, F, and Ga have nearly equal accuracies,

[+]The approximate Palm ratios between the coefficients in the interaction terms were also found[I2] in the polylinear expansions for the formation enthalpies of alkanes and amines. We found recently, however, that these ratios disappear with replacement of the "zero point" used in Ref. I2.

one would expect good linear relationships between the scales X_A, X_B and σ^+. The actual ones are presented in Table 4 and they are rather satisfactory.

Table 4

Relationships y = a + bx Between the Substituent Parameters X_A, X_B and σ^+[a]

y	x	a	b	n	r	s_0(s%[c])
X_B	X_A	-2.742∓0.210	0.247∓0.038	5	0.966	0.41
X_A	σ^+	0.427∓0.724	6.457∓0.741	4[b]	0.977	I.5I(I0.6)
X_B	σ^+	-2.436∓0.088	-I.683∓0.213	I2[b]	0.949	0.22(6.I)

[a]The correlations are found excluding the points for the substituent H.The latters,however,are within the corresponding "uncertainty corridors". [b]Points for p-MeØ groups are ruled out as significant outliers. [c]$s\% = 100 s_0/\Delta y$, Δy is a variation interval for y.

6. The regressions of Table 3, i.e. A, D, E, F and particularly Regs. Ga, H, and I have strong interpolating prediction powers.However, the more reliable ones of those regressions are, in our opinion, Regs. A, D, and E. They are based on the scale X_A and describe the wide range of pK_R+ values.At the same time, no experimental points are found that deviate significantly from these regressions. In the regressions based on the scale σ^+ the estimates for $a_0 + a_3$ may be biased to a certain extent; See the intercept for the correlation of X_A vs σ^+ in Table 4. Extending the regression to diarylcarbinols, one finds also some biasings in these estimates (Cf. Regs. Ga and I). The estimation of constant σ^+ for substituent H is a formal manipulation only,since it contradicts the "physical" meaning[10] of these constants.

7. It is possible, on the basis of Reg. I0 and the X_A-value for H, to estimate roughly pK_R+'s for both benzyl alcohol (-23.5) and methanol (-38.5). While the first estimate seems to be plausible, the second one appears to be too unreliable, because it depends strongly on slight variations in X_A(H) due to far extrapolation of the equation found.

References

1. Istomin B.I., Eliseeva G.D., & Finkelstein B.L., This 15, 511 (1978)
2. Palm V.A., Fundamentals of Quantitative Theory of nic Reactions (in Russian), "Khimiya", Leningra 1977
3. Rudakov E.S., Doklady akademii nauk SSSR, 241, 635 (1
4. Istomin B.I.& Baransky V.A., This J., 15, 291 (1978)
5. Istomin B.I., This J., 15, 216 (1978)
6. Istomin B.I.& Baransky V.A., This J., 15, 204 (1978)
7. Bethell D. & Gold V., Carbonium Ions. An Introduction demic Press, 1967; Russian Translation, "Mir", Moscow, 1970
8. a).Deno N.C., Jaruzelski J.J. & Schriesheim A., J.Org 19, 155 (1954); b)J.Am.Chem.Soc., 77, 3044 (1955); c) no N.C. & Schriesheim A., J.Am.Chem.Soc., 77, 3051 (1 d) Deno N.C. & Evans W.I., J.Am.Chem.Soc., 79, 5804 (
9. Ritchie C.D., Sager W.F. & Lewis E.S., J.Am.Chem. Soc 84, 2349 (1962); See also the references therein.
10. Hine J., Structural Effects on Equilibria in Organic mistry, Wiley & Sons, 1975
11. Mindl J. & Večeřa M., Coll. Czech. Chem.Communs., 36, (1971); 37, 1143 (1972)
12. Istomin B.I., The Thesis, Tartu State University, Tar 1973; Istomin B.I. & Palm V.A., Reakts. sposobn. org. 10, 537 (1973)
13. Istomin B.I.,& Lipovich V.G., This J., 11, 933 (1975)

Comparative Investigation of the Nucleophilic Substitution Reactions at Phosphoryl and Carbonyl Centers. 5. Combined Effect of Structure and Solvent on Alkaline Hydrolysis of Ethyl Benzoates[+]

B.I.Istomin*, B.N.Bazhenov, G.D.Eliseeva & B.L.Finkelstein

Petroleum Synthesis Institute at Irkutsk State University, P.O. Box I665, Irkutsk, 664033

Received April 15, 1979

Analysis of the literature data reveals that combined effect of the acyl substituent and solvent on the alkaline hydrolysis rate constants k_2 for ethyl benzoates in aqueous ethanol, dioxane, acetone, and sulfonale at 25°C is accurately described (unlike aqueous DMSO) by non-additive equation (3). The physical meaning of the cross-term in this equation is discussed.

In Ref. 2 it has been found that combined effect of acyl structure, temperature, and solvent (i.e. composition of organo-aqueous binary mixtures) on reactivities of m,p-substituted ethyl benzoates (EB's) in their alkaline hydrolysis fits accurately the equation

$$\log k = a_0 + a_I S + a_2 t + a_3 \sigma + a_4 St + a_5 S\sigma + a_6 t\sigma \quad (I)$$

$t = 10^3/T$, °K, if one defines operationally the medium effect measure S as follows

$$S = \log k_H^{25}(\text{i-th mixture}) - \log k_H^{25}(H_2O) \quad (2)$$

The coefficients $a_I \div a_6$ are found[2] to be the same for various mixtures of H_2O with ethanol, dioxane, acetone and sulfolane, but these coefficients differ from those found in aqueous DMSO. Hence, the rate constants k_2 for alkaline hydrolysis of EB's at

[+]For Part 4 see Ref. I.

any temperature and in all mixtures mentioned, but H_2O -DMSO, would follow the general equation

$$\log k = b_0 + b_I S + b_2 \sigma + b_3 S \sigma \qquad (3)$$

with b_3 being independent of the mixture organic component. Similar equation

$$\log k = b'_0 + b'_I S' + b'_2 \bar{\sigma}^\circ + b'_3 S' \bar{\sigma}^\circ$$

describes[3] the combined effect of solvent and the leaving group structure on alkaline hydrolysis of m,p-substituted phenyl acetates (PA's) in aqueous ethanol,dioxane,acetonitrile or acetone;S' is a formal measure of solvent effect on the hydrolysis of PA's which is derived[3] analogously to the parameter S.The coefficient b_3 in the last equation depends,however,on an organic component in the solvent mixture, i.e. in the above mixtures the general equation for the hydrolysis of PA's is absent.This fact forces us to analyze more thoroughly the experimental data for alkaline hydrolysis of EB's to check the well-groundedness of our earlier conclusions[2].

Table I collects the data for alkaline hydrolysis of EB's in various mixtures at 25°C; those data are from Ref.4. In every solvent system the rate constants k_2 are actually described (see Table 2, Regs. A - D) by Equation (3) when one defines parameters S according to (2).The coefficients b_0 as well as b_2 in Regs. A - D are equal, within their uncertainties, and are in good agreement with log k_0 and ρ respectively in Hammett equation (6) found for the reaction in aqueous solution (see Table 4). All estimates of b_I do not differ significantly from their theoretical value, I.00. Being slightly different, coefficients b_3 in those regressions do not differ within their uncertainties $t_{0.05}s(b_3)$, i.e. one should assume that the magnitude of b_3 does not depend on an organic component in the mixtures considered, except that of H_2O - DMSO. Reg. F supports strongly that assumption. Ruling out the rate constants measured in aqueous solution, one finds Reg. E. Its statistical indices are rather comparable with

Table I

Experimental Data[4], log k_2^{25}, for Alkaline Hydrolysis of Ethyl Benzoates

Substituent	Solvent System and Its Composition[a]											
	H_2O	EtOH-H_2O		An - H_2O		D - H_2O		TMS - H_2O		DMSO - H_2O		
		23.6	68.9	I5.I	28.3	I2.4	I7.4	35.8[b]	65.9[b]	32.0	59.0	82.8
H	-I.48	-2.75	-3.2I	-2.33	-2.57	-2.I7	-2.29	-2.07	-2.30	-I.44	-0.7I	0.06
p-Me	-I.69	-3.I6	-3.58	-2.73	-2.92	-2.58	-2.72			-I.76	-I.2I	-0.33
m-Cl	-0.89	-2.08	-2.3I	-I.64	-I.75	-I.52	-I.65	-I.4I	-I.59			
p-Cl	-I.I5	-2.26	-2.63	-I.84	-I.96					-0.79	-0.I2	0.83
p-Br	-I.I2		-2.54		-I.80							
m-NH_2	-I.58		-3.5I		-2.78							
p-NH_2	-2.50	-4.I3	-4.88	-3.76	-4.06	-3.57	-3.77	-3.39	-3.78			
m-NO_2	-0.40							-0.79	-0.89			
p-NO_2	-0.23	-0.9I	-I.25	-0.60	-0.6I		-0.50	-0.6I	-0.67	0.44		

[a]The abbreviations An and D denote[3] acetone and dioxane. The binary mixture compositions are in mole per cents of organic component. [b]For aqueous acetone weight per cents are used.

Table 2

Coefficients & Statistics of Equation (3) for Alkaline Hydrolysis of EB's in Different Solvents[a]

Regs.	A	B	C	D	E	F	H
Coefs. & Sts.	EtOH-H_2O	An-H_2O	D-H_2O	TMS-H_2O	without water	all mixtures	DMSO
b_0	-I.45I	-I.459	-I.452	-I.47I	-I.576	-I.50I	-I.449
	∓0.0I5	∓0.0I0	∓0.0I8	∓0.0II	∓0.029	∓0.0I8	∓0.039
b_I	I.000	0.992	I.093	I.082	0.9I7	0.980	I.007
	∓0.0I6	∓0.032	∓0.045	∓0.027	∓0.030	∓0.020	∓0.I00
b_2	I.522	I.524	I.5I8	I.538	I.745	I.6I7	2.375
	∓0.042	∓0.054	∓0.054	∓0.030	∓0.065	∓0.045	∓0.I00
b_3	-0.565	-0.755	-0.840	-0.686	-0.436	-0.550	0.39I
	∓0.036	∓0.072	∓0.098	∓0.05I	∓0.062	∓0.047	∓0.I7I
n	22[b]	22[c]	I8	I8[d]	44[e]	53[e]	I0[h]
R	0.999	0.998	0.998	0.999	0.998	0.998	0.998
S_0	0.068	0.07I	0.070	0.037	0.069	0.077	0.072

[a]Every regression except Reg.E includes 9 log k_2 - values measured in water; see Table I. The σ-constants of McDaniel & Brown are from Ref.5. For all regression coefficients the corresponding standard deviations are listed in the table. [b]The point for m-Cl in aq.EtOH(23.6%) is excluded as a significant outlier. [c]Without significantly deviated point for p-Br in aq. acetone (28.3%). [d]The rate constant for m-NH_2 in H_2O is excluded. [e]Without significantly deviated points for m-Cl (aq.EtOH, 23.6%), p-Br and p-NO_2 (aq. acetone, 28.3%). These deviations are significant at the accepted risk level of 5% but are small. Their including in the regression analysis does not alter significantly $b_0 \div b_3$ and their statistics as well as the multiple regression coefficient R and the regression statdard S_0. [h]Including no rate constants measured in H_2O.

those of Reg. F, whereas its coefficients $b_0 \div b_3$ are slightly biased since that exclusion appears to increase non-orthogonalities in the corresponding matrix of variables. Coefficients b_2 and b_3 found for DMSO-H_2O differ significantly from their counterparts in Regs. A - D. That result confirms the conclusion[2] that it is impossible to describe within the same Eq. (3) the data for this system and those measured in other mixtures considered.

Table 3 lists the results of analysis of the data of Table 1 by the equation

$$\log k = b_0 + b_1 S + b_2 X + b_3 SX \qquad (4)$$

In that equation, the "intrinsic" scales[6,7] are used both for solvent effect (S) and for the structural effect (X)

$$X = \log k_X(H_2O) - \log k_H(H_2O) \qquad (5)$$

on the process under investigation. According to PPL[8], the scales S and X place on the coefficients $b_0 \div b_2$ in the equation the following restraints: $b_0 = \log k_H(H_2O) = -1.48$ (see Table 1) and $b_1 = b_2 = 1.00$. The unbiasing estimates found for $b_0 \div b_2$ in Regs. A - D of Table 3 confirm[6,7] significance of coefficient b_3 in these regressions. Exclusion of the non-additive term leads to the dramatically biased estimates of $b_0 \div b_2$ in all binary systems except that of DMSO. In Regs. A - D estimates of b_3 also do not differ, within their uncertainties, i.e. its value seems to be independent of organic component in the corresponding solvents. In Reg.F, that descibes all rate constants except those measured in aq. DMSO, coefficients $b_0 \div b_2$ also do not differ from their theoretical values. Hence, Regs. A - D appear to be the special cases of the more general regression F. Being found after exclusion of the rate constants measured in H_2O, Reg. E has significantly biased coefficient b_I, while its other coefficients differ rather insignificantly from the corresponding ones in Reg. F. In Reg.H for aq. DMSO, b_3 is insignificant whereas b_2 differ drastically from I.00.

If the combined effect of solvent and acyl structure on the

Table 3

Coefficients and Statistics of Equation (4) for Alkaline Hydrolysis of EB's in Different Solvents[a]

Regs.	A	B	C	D	E	F	H
Coefs. & Sts.	EtOH-H_2O	An-H_2O	D-H_2O	TMS-H_2O	without water	all mixtures	DMSO
b_0	-I.477	-I.484	-I.480	-I.480	-I.572	-I.5I7	- I.357
	∓0.0I6	∓0.0I6	∓0.0I6	∓0.008	∓0.03I	∓0.0I7	∓ 0.076
b_I	I.009	I.006	I.092	I.079	0.948	0.995	0.999
	∓0.0I5	∓0.026	∓0.039	∓0.02I	∓0.030	∓0.020	∓0.076
b_2	0.997	0.999	0.998	0.994	I.III	I.048	I.48I
	∓0.028	∓0.029	∓0.03I	∓0.0I5	∓0.045	∓0.028	∓0.II4
b_3	-0.354	-0.47I	-0.50I	-0.429	-0.293	-0.349	-0.083
	∓0.024	∓0.038	∓0.054	∓0.026	∓0.043	∓0.029	∓0.I60
n	22	22	I8	I9	44	53	I0[b]
R	0.999	0.999	0.999	0.999	0.998	0.998	0.992
S_0	0.056	0.057	0.060	0.030	0.073	0.07I	0.I30

[a]In all regressions of this table, except Reg.D, the same points as those of the corresponding regressions of Table 2 are excluded. [b]Without the data for H_2O.

alkaline hydrolysis of EB's in aqueous ethanol, dioxane, acetone, and in aqueous sulfolane actually follow the general equation (3), then reaction constants ρ in Hammett equation

$$\log k = \log k_0 + \rho\sigma \qquad (6)$$

for those systems of any composition should depend linearly on the solvent parameter S with a slope being equal to the coefficient b_3 of equation (3). It is also evident, that in accordance with equation (3), $\log k_2$ for any EB should depend linearly on $\log k_2$ for unsubstituted EB, when those rate constants are measured in the solvent of the same composition, i.e.

$$\log k\,(X) = c_0 + c_I \log k\,(H) \qquad (7)$$

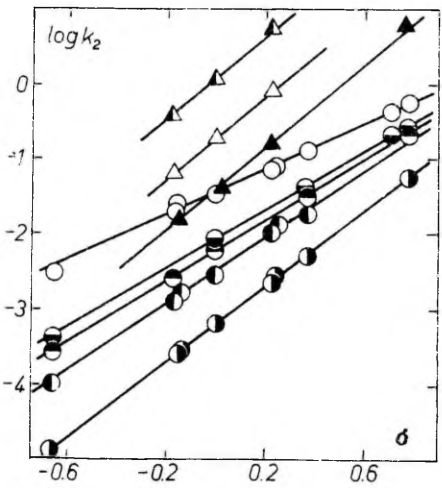


Fig. I. The Hammett plots for alkaline hydrolysis of EB's in H_2O (○), in 65.9% aq. TMS (◒), I2.7% aq. dioxane (◓), in 28.3% aq. acetone (◐) in 68.9% aq. EtOH (◑) as well as in 32% (▲) 59% (△) and in 82.8% (◭) aq. DMSO.

All solvent systems considered, except that of aq. DMSO, should obey the last equation. The linear relationship should then be found between coefficients c_I for different EB's and the corresponding σ. Its slope will also be equal to b_3 in Eq. (3). Figs. I and 2 illustrate equations (6) and (7). It is noteworthy, that all straight lines in these figures are non-parallel, except those for aq. DMSO, and tend to cross in the same (isoparametrical[8-10]) point. Tables 4 and 5 collect the coefficients and statistics of these equations found on the basis of the data in Table I. Their coefficients ρ and c_I are seen to depend strongly on the solvent and the substituent, respectively. Equation (7) has good statistics for all substituents except p-NO_2. The poor result for that one appears to be related to some uncertainties in the data used (see Table I). The magnitude of ρ is in satisfactory correlation with the k_2-values for unsubstituted ester measured in the same solvents

$$\rho = (0.815 \mp 0.202) + (-0.551 \mp 0.084)\log k_H \qquad (8)$$
$$n = 9 \quad r = 0.927 \quad s_0 = 0.114$$

Those log k_2 - values are linearly related to the correspond-

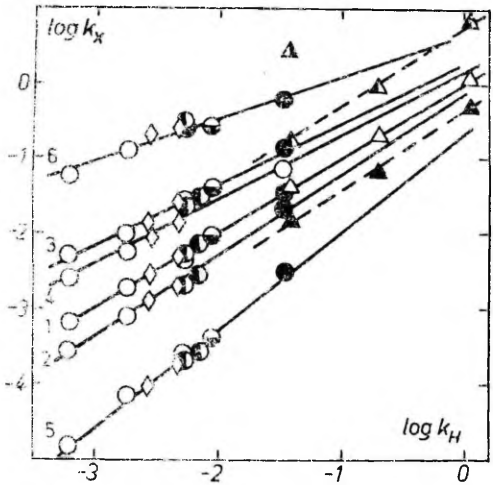


Fig. 2. Relationships between log k_X of m,p-substituted EB's (X = I. H; 2.p-Me; 3.m-Cl; 4. p-Cl; 5.p-NH_2 and 6.p-NO_2) and log k_H for unsubstituted ester in H_2O (●) and in mixtures of water with EtOH (○), acetone (◇), dioxane (◐), sulfolane (◒), and with DMSO (△, ◭, ◮, ▲). The points △, ▲, ◭ and ◮ correspond to EB's with X = : H, p-Me, p-Cl and p-NO_2, respectively.

ing parameters S. The slope of that correlation agrees well with b_3 in Reg.F of Table 2. The good correlation exists also between c_I and σ constants for the corresponding substituents

$$c_I = (0.987 \pm 0.012) + (-0.535 \pm 0.026)\sigma \qquad (9)$$
$$n = 9 \quad r = 0.992 \quad s_0 = 0.034$$

Its slope is equal as well to b_3 in Reg. F of Table 2.

Thus, the above results strongly confirm our earlier conclusion that, at any constant temperature, the combined effect of reaction medium and structure of substituent on the reactivities of EB's in their alkaline hydrolysis is describeable with good accuracy by the same equation (3) in various mixtures of ethanol, acetone, dioxane, and sulfolane with water. That fact appears to show some deep similarities in the effects of those mixtures and water itself on the process of interest. On the other hand, a mechanism of an effect of aq. DMSO on that process is apparently different.

Table 4

Parameters of Hammett Equation (6) for Alkaline Hydrolysis of EB's

Org. component[a]	Mixture Compos.	S	log k_0	ρ	n	r	s_0
—	H_2O[b]	0	-I.45I±0.0I9	I.52I±0.043	9	0.997	0.055
EtOH	23.6	-I.27	-2.749±0.045	2.200±0.097	6	0.996	0.I07
	68.9	-I.73	-3.I82±0.0I9	2.495±0.047	8	0.999	0.053
An	I5.I	-0.85	-2.348±0.026	2.I7I±0.056	6	0.998	0.06I
	28.3	-I.09	-2.490±0.035	2.369±0.086	8	0.996	0.097
D	I2.4	-0.69	-2.23I±0.027	2.00I±0.070	4	0.998	0.052
	I7.4	-0.8I	-2.329±0.049	2.228±0.099	5	0.997	0.I08
TMS	35.8	-0.59	-2.II2±0.0I7	I.908±0.029	5	0.999	0.055
	65.9	-0.82	-2.356±0.024	2.I25±0.04I	5	0.999	0.049
DMSO	32.0	0.04	-I.379±0.035	2.353±0.084	4	0.998	0.060
	59.0	0.77	-0.732±0.0I6	2.738±0.096	3	0.999	0.027
	82.8	I.54	0.I3I±0.05I	2.947±0.308	3	0.995	0.087

[a]See Table I. [b]For the reaction in water.

Table 5

Coefficients and Statistics of Equation (7)

Substituent in EB	σ^a	c_0	c_I	n	r	s_0
H	0.00	0.00[b]	I.00[b]			
p-Me	-0.I7	-0.I74±0.I25	I.08I±0.05I	7	0.994	0.067
m-Cl	0.373	0.309±0.I04	0.832±0.043	9	0.990	0.058
p-Cl	0.227	0.I42±0.I32	0.855±0.052	5	0.994	0.066
p-Br	0.232	0.II5±0.354	0.800±0.I40	3	0.985	0.I73
m-NH_2	-0.I6	0.073±0.026	I.II4±0.0I0	3	0.999	0.0I3
p-NH_2	-0.66	-0.649±0.I59	I.322±0.066	9	0.999	0.089
m-NO_2	0.7I	0.498±0.098	0.6I0±0.050	3	0.997	0.030
p-NO_2	0.778	0.648±0.205	0.556±0.085	9	0.937	0.II3

[a]According to McDaniel & Brown[5]. [b]According to the definition of the scale S; See Eq. 7.

Rate and equilibrium constants of any reaction are believed[8,11,12] to depend on those factors only which effects on free energies of initial and transition (or final) states of that reaction are sufficiently different. The general free energy change, $\triangle\triangle F_{tot}$, in the alkaline hydrolysis of various EB's in different solvents may be then considered as the sum of structural ("inner") and solvation ("outer") terms

$$\triangle\triangle F_{tot} = \triangle\triangle F_{st} + \triangle\triangle F_{sol} \qquad (10)$$

The sum reflects quantitative differences in interactions between the substituent and the reaction center in initial and transition states ($\triangle\triangle F_{st} \neq 0$) of the reaction[+] as well as in solvations of those states ($\triangle\triangle F_{sol} \neq 0$). The statistically significant cross-term $b_3 S\sigma$ in equation (3) shows that the term $\triangle\triangle F_{sol}$ is dependent on the acyl substituent

$$\triangle\triangle F_{sol} = -2.303RTS(A + B\sigma) \qquad (11)$$

A and B are constants and S is the solvent parameter. Hence, the non-zero term $b_3 S\sigma$ in equation (3) should appear only when $B \neq 0$, i.e. when the effects of the substituent on the solvation contributions $\triangle\triangle F^{\neq}_{sol}$ and $\triangle\triangle F^{in}_{sol}$ in the free energies of the transition and initial states of the process[++] have different intensities, being similar in their nature at the same time.

The statistical data handling was carried out on "Odra-1304" (Poland) and "Nairi-S" computers by the multiple regression programs based on Refs. 2 and 14.

References

1. Eliseeva G.D., Istomin B.I. & Kalabina A. V., Zh. obs. khim., 48, 1901 (1978)
2. Istomin B.I., Finkelstein B.L., Sukhorukov Yu.I. & Donskhikh V.I., This J., 14, 492 (1977)

[+] The limiting step of that process is believed[2,13] to be a formation of the tetrahedral addition intermediate.

[++] That is, when those effects are describeable by the same set of constants; σ or σ^0, for example.

3. Istomin B.I., Bazenov B.N., Eliseeva G.D. & Finkelstein B.L., This J., 16 , 196 (1979)
4. Tables of Rate and Equilibria Constants of Heterolytic Organic Reactions, Ed.by V.A.Palm, Vol. I, Part 2, VINITI, Moscow, 1975
5. Zhdanov Yu.A.& Minkin V.I., Correlation Analysis in Organic Chemistry (In Russian), Rostov State University, Rostov-na-Donu, 1967
6. Istomin B.I., & Baransky V.A., This J., 15, 215 (1978)
7. Istomin B.I., This J., 15, 226 (1978)
8. Palm V.A., Fundamentals of Quantitative Theory of Organic Reactions, (in Russian), "Khimiya", Leningrad, 1977
9. Palm V.A.& Istomin B.I., This J., 6, 427 (1969)
10. Istomin B.I., Pivovarov S.A., Selivanov V.F., Gidaspov B.N., & Istomina S.N., This J., 12, 289 (1975)
11. Jencks W.P., Catalysis in Chemistry and Enzymology, McGraw-Hill Book Co., New York, 1969; Russian Translation, "Mir", Moscow, 1972; Jencks W.P.,& Gilchrist M., J.Am.Chem.Soc., 90, 2622 (1968)
12. Hine J., Structural Effects on Equilibria in Organic Chemistry, J.Wiley & Sons, New York, 1975
13. Ritchie C.D., J.Am.Chem.Soc., 97, 1170 (1975)
14. Draper N., & Smith G., Applied Regression Analysis; (Russian Translation), "Statistika" Moscow, 1973

Comparative Investigation of the Nucleophilic Substitution Reactions at Phosphoryl and Carbonyl Centers. Part 6. Combined Effect of Structural and Medium Factors on Alkaline Hydrolysis of Aryl Acetates in Organo-Aqueous Mixtures

B.I.Istomin*, B.N.Bazhenov, G.D.Eliseeva & B.L.Finkelstein

Petroleum Synthesis Institute at Irkutsk State University, P.O. Box 1665, Irkutsk, 664033

Received April 15, 1979

The alkaline hydrolysis kinetics for four arylacetates is investigated spectrophotometrically at 25° in various mixtures of water with dioxane, acetonitrile, and, partially, with acetone. The non-additivity in the effects of the leaving group structure and medium on this process is described adequately by Eq.(3). The extent of non-additivity of these factors is found to depend on the nature of an organic component in a solvent system. The isoparametricity phenomenon, i.e. a reverse of a solvent effect on the reaction rate with a change in the leaving group structure, is observed in aqueous dioxane and in aqueous acetone. Its reasons are discussed.

According to Refs.I-3, the LFE relationships[4,5] are well applicable to a solvent effect on alkaline hydrolysis of the esters of carbon acids. At the same time, structure of the ester leaving group or its acyl part and solvent affect the process non-additivily[I-3]. For example, the alkaline hydrolysis rate constants of ethyl benzoates (EB's) in various binary mixtures fit accurately the equation[I,3]

$$\log k_{ij} = a_0 + a_1 S_j + a_2 \sigma_i + a_3 \sigma_i S_j \qquad (I)$$

In Eq. (I) S_j is the medium effect measure that has been derived[3+], in accordance with the polylinearity principle (PPL)[4], from the rate constants for unsubstituted EB in the j-th mixture and in water

$$S_j = \log k_H(\text{j-th mixture}) - \log k_H(H_2O) \qquad (2)$$

In Eq.(I) a_3 is found to be independent[I] of a solvent, when EB's have been hydrolyzed in aqueous ethanol, dioxane, acetone and in aqueous sulfolane.

Alkaline hydrolysis of phenyl acetates (PA's) in aqueous ethanol fits [2] a similar equation

$$\log k_{ij} = b_0 + b_1 S'_j + b_2 \bar{\sigma}^o_i + b_3 S'_j \bar{\sigma}^o_i \qquad (3)$$

when one defines the medium effect measure S'_j in the similar way. However, it is impossible to compare the characters of combined effects of structural and solvent factors on the alkaline hydrolysis of PA's and EB's, since there are no experimental data for the first series in different solvent mixtures. The present paper deals with kinetic investigations of alkaline hydrolysis of PA's at 25° in various mixtures of water with dioxane (D), acetonitrile, and, partially, with acetone (An). The measurements are done according to the previuosly proposed way[8,9] of multifactorial experimentation.

Experimental

The reaction kinetics is studied spectrophotometrically under pseudo-first-order conditions with sodium hydroxide in a large excess. Apparatus and materials used as well as the experimental conditions of the measurements and some special features of mathematical and statistical treatments of the data were described previosly[2,10,11]. Solvents are purified by the known methods[12]. The sodium hydroxide solutions in

+ This parameter is similar to a medium operator $\delta_M \Delta F$ that have been used[5] by Leffler and Grunwald.

Table I

Bimolecular Rate Constants k_2 ($l\ mole^{-1} sec^{-1}$) of Alkaline Hydrolysis of $CH_3C(O)OC_6H_4X$-m,p at 25°

X	Solvent composition[a]	k_2
H_2O - Dioxan		
p-Me	50	0.5I9±0.004
	70	0.398±0.002
	80	0.389±0.004
H	20	I.093±0.0II
	40	0.894±0.0I4
	50	0.796±0.0I7
	60	0.632±0.040
	70	0.562±0.003
	80	0.544±0.006
p-Br	50	I.930±0.026
	70	I.706±0.0I2
	80	I.730±0.0I3
p-NO_2	20	I0.75I±0.095
	40	II.963±0.II5
	50	I2.878±0.I40
	60	I3.752±0.II4
	70	I5.620±0.I05
	80	I7.524±0.I99
m-Me	50	0.504±0.006
p-MeO	50	0.6I0±0.005
H_2O - MeCN		
p-Me	30	0.402±0.004
	70	0.I56±0.003
H	30	0.546±0.006
	70	0.244±0.00I
p-Br	30	I.093±0.007
	70	0.604±0.007
p-NO_2	30	5.597±0.04I
	70	3.777±0.029
H_2O		
p-Me	0	I.048±0.0I4[b]
m-Me	0	I.I09±0.04I[c]
m-MeO	0	I.667±0.037[b]
p-OMe	0	I.I39±0.0I9[b]
H	0	I.42I±0.0I3[d]
p-Br	0	2.694±0.073[b]
p-NO_2	0	9.93I±0.I57[b]
H_2O - EtOH		
p-Me	50	0.98I±0.0I8[b]
	90	0.964±0.0I7[b]
H	50	I.296±0.053[b]
	90	I.370±0.034[b]
p-Br	50	3.328±0.074[b]
	90	4.705±0.064[b]
p-NO_2	50	24.28±0.8I[b]
	90	54.97±0.98[b]
H_2O - Me_2CO (An)		
p-Me	6I.6	-0.494[e,f]
H	6I.6	-0.298[e,h]
	70	-0.498[e,g]
m-Me	6I.6	-0.389[e,h]
m-NO_2	6I.6	0.774[e,h]
p-NO_2[k]	40	9.728±0.057
	6I.6	II.I35±0.057
	70	I2.28I±0.I03

[a]The organic component content in a solvent mixture; in (v/v) [b]Ref. 2. [c]Ref.IO. [d]Our more accurate result found from 43 values of k_I, independent measurements done recently in our laboratory, which are measured at 6 different concentrations of NaOH. The result listed in Table seems to be more reliable than those from Refs. 2 and II. This value is also in better agreement with Ref.IO. [e]We give here log k. [f]These values of log k are estimated from the corresponding Arrhenius relationships based on the data[I4,I5,I7]. [g]log k is estimated from the Arrhenius relationship based on the data[I4,I6]. [k]The spectrophotometric technique used for the kinetic studies is applicable to this ester only.

binary mixtures are prepared before each series of measurements from its aqueous solutions of the known concentrations, absolute organic component, and from binary solvent mixture of the same composition. For every ester, kinetic curves were recorded three or more times at three or four sodium hydroxide concentrations. The pseudo-first-order rate constants, k_I, are found to be unchangeable up to 7-8 half--lives for all esters.These constants are in good linear dependence,with zero intercepts,on the sodium hydroxide concentrations used. These facts indicate bimolecular character of the reaction and the absence of noticeable spontaneous hydrolysis under experimental conditions. Our results, i.e. the bimolecular rate constants k_2 with their standard errors, are listed in Table I. Our earlier data[2] measured for the series in water and in aqueous ethanol as well as the data[I4] for aqueous acetone are also presented in the table. The statistical data handling is carried out on "Odra-1304" (Poland) and "Nairi-S" computers by the multiple regression analysis programs[I,7,I5].

Results and Discussion

An Effect of One Variable. The leaving group effect on the hydrolysis of PA's in all mixtures considered follows accurately the equation (see Table 2 and Fig.I)

Table 2

Coefficients and Statistics of Equation (4)[a]

Medium	Solvent composition[b]	log k_0	ρ	n	r	s_0
H_2O	0	0.I5I±0.0I3	0.947±0.037	7	0.9962	0.033
H_2O-D[c]	50	-0.095±0.026	I.353±0.067	6[e]	0.9952	0.060
		-0.090±0.0I2	I.35I±0.026	4[f]	0.9996	0.02I
	70	-0.205±0.024	I.569±0.05I	4	0.9989	0.04I
	80	-0.2I0±0.024	I.628±0.052	4	0.9989	0.04I
H_2O-	30	-0.252±0.006	I.II5±0.0I3	4	0.9998	0.0I0
MeCN	70	-0.604±0.0I9	I.335±0.040	4	0.999I	0.032
H_2O-	6I.6	-0.324±0.04I	I.445±0.076	5	0.9959	0.076
An	70	-0.498[d]	I.773[d]			
H_2O-	50	0.I54±0.02I	I.375±0.045	4	0.9989	0.036
EtOH	90	0.I93±0.030	I.733±0.063	4	0.9987	0.050

[a]Constants $\bar{\sigma}^o$ are from Ref.I8; for p-Br $\bar{\sigma}^o = \sigma^o$ is assumed(See Ref.19). [b]The organic component content in a solvent mixture; in (v/v). [c]D and An denote dioxane and acetone, respectively. [d]The result is based on two points only. [e]For all substituents in leaving groups. [f]For groups p-Me, H, p-Br,and p-NO_2 (See Table I).

$$\log k = \log k_0 + \rho\bar{\sigma}^o \qquad (4)$$

The LFE principle is also applicable, within every binary system, taken separately, to a solvent effect on the reaction, i.e. a linear relationship

$$\log k(X_2) = c_0 + c_I \log k(X_I) \qquad (5)$$

is observed between the log k values of any pair of PA's in the same mixtures. The data for unsubstituted PA (See Fig.3) and p-Me-PA (See Fig.2) in 80% dioxane deviate from such regressions, when X_I = p-NO_2. The deviations may be

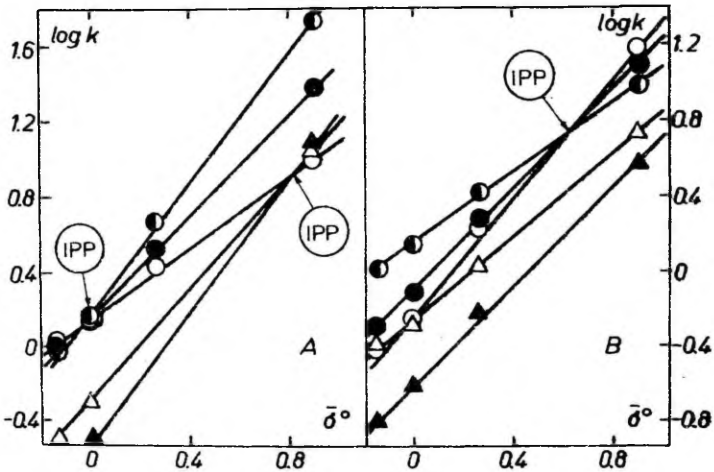


Fig. I. Plots of log k for alkaline hydrolysis of PA's vs $\bar{\sigma}^{\circ}$ for the leaving group substituents in [A] water (○), 50% (●) and 90% (◐) aq. EtOH, 61.6% (△) and in 70% (▲) aq. acetone as well as in [B] water (◐), 50% (●) and in 70% (◐) aq. dioxane, in 30% (△) and in 70% (▲) aq. acetonitrile. IEP is an isoparametric point.

related to unapplicability of the LFER principle in these cases[+]. Coefficients ρ and c_I (See Figs. I-3 and Tables 2, 3) in equations (4) and (5) depend strongly on the solvent composition and on the leaving group structure, respec-

[+]One can assume also that the LFER principle is actually unappicable to the solvent effect in 80% dioxane on p-NO_2-PA because good correlations of type (5) are observed for unsubstituted PA, p-Br-PA, and p-Me-PA within the whole interval of the solvent system compositions.

Table 3

Coefficients and Statistics of Equation (5)

Mixture	X_2	X_I	c_0	c_I	n	r	s_0
H_2O-EtOH	H	p-NO_2	0.17±0.07	-0.02±0.05	3	0.421	0.026[a]
	p-Br	p-NO_2	0.09±0.08	0.33±0.05	3	0.986	0.028
	p-Me_2	p-NO_2	0.07±0.02	-0.05±0.01	3	0.957	0.008
H_2O-D	p-NO_2	H	1.06±0.01	-0.55±0.07	7	0.962	0.026[b]
	p-NO_2	H	1.06±0.01	-0.47±0.04	6	0.987	0.013[c]
	p-NO_2	H	1.07±0.02	-0.48±0.03	4	0.977	0.028[d]
	p-NO_2	H	1.07±0.00	-0.48±0.03	3	0.998	0.008[e]
	p-Br	H	0.35±0.01	0.48±0.04	4	0.992	0.015[f]
	p-Me	H	-0.15±0.02	1.04±0.08	4	0.995	0.025[f]
H_2O-MeCN	p-Me	H	-0.13±0.02	1.08±0.05	3	0.999	0.028
	p-Br	H	0.29±0.02	0.85±0.06	3	0.998	0.030
	p-NO_2	H	0.91±0.01	0.55±0.03	3	0.998	0.016
H_2O-An	p-NO_2	H	1.01±0.01	-0.14±0.02	3	0.986	0.011

[a]Since $\hat{\sigma}^o \simeq \bar{\sigma}^o(H)$, the rate constant k_2 for the unsubstituted ester is practically independent of the organoethanol mixture composition; see Ref.2. [b]For all dioxane-water mixtures; see Table I, and Fig. 3. [c]Without the point for 80% dioxane. [d]For water, 50-, 70-, and for 80% aq. dioxane. [e]Without the point in 80% aq.dioxane. [f]For water, 50-, 70- and for 80% aq.dioxane.Exclusion of the point for 80% mixture does not improve the correlation statistics.

tively, i.e. the combined effect of the two factors on reactivities of the esters in the reaction studied is non-additive. The striking confirmation for such way of their effect is the isoparametricity phenomenon[4,6,7] (IPP) observed in alkaline hydrolysis of PA's in aqueous dioxane (See Figs. 1 and 2). With increasing dioxane content in the solvent mixture, the hydrolysis rate constants for p-NO_2-PA and for PA's with X = p-Me, H or p-Br change in opposite directions (See Table I). IPP is also observed in aqueous acetone

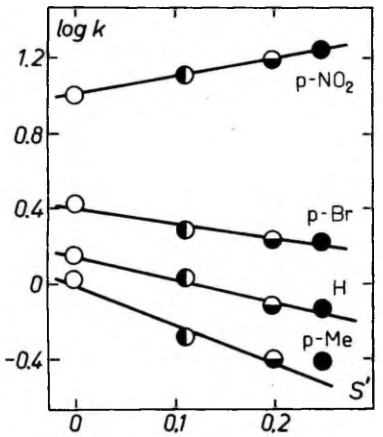


Fig.2. Plots of log k for PA's in aq.dioxane vs. the parameter S'_j = log k(p-NO_2, j-th mixture) - log k(p-NO_2, H_2O). Points ○ , ◐ , ◒ and ● correspond to the reaction in water, 50%, 70% and in 80% mixtures, respectively.

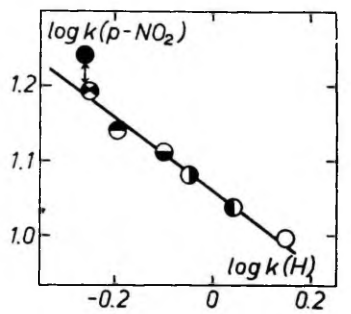


Fig.3. Plot of log k for p-NO_2-PA vs. log k for unsubstituted ester in variuos mixtures of water with dioxane. The points ○ , ◐ , ◑ , ◒ , ◓ , ⊗, and ● correspond to a reaction in water, 20, 40, 50, 60, 70 and in 80% mixtures, respectively.

(See Fig.I) and in aqueous EtOH[2].

Cross-Correlations. As it is seen from Table 4, log k values for PA's in every mixture fit accurately equation (3). For comparison we use here two "inner" scales S'_j for a medium effect. They are based on the data for unsubstituted PA (See Regs. B, C, and D in Table 4) and for p-NO_2-PA (Regs. A-a, B-a, and C-a) . In all multiple regres-

Table 4

Coefficients and Statistics of Equation (3) for Different Binary Systems

Reg.	Mixture	b_0	b_I	b_2	b_3	n	R	S_0	$\hat{\sigma}^{ok}$
A-a	H_2O-EtOH	0.I52∓0.0I9	0.044∓0.039	0.95I∓0.040	I.06I∓0.082	I2[a,h]	0.9987	0.034	-0.44∓0.04
B	H_2O-D	0.I53∓0.0I7	0.902∓0.054	0.945∓0.036	-I.6I2∓0.II4	I6[b,c]	0.9989	0.030	0.56∓0.05
		0.I53∓0.0I5	0.9I4∓0.056	0.949∓0.032	-I.555∓0.II9	I2[c,d]	0.999I	0.027	0.59∓0.06
B-a		0.I30∓0.024	-I.552∓0.I43	0.980∓0.05I	2.829∓0.304	I6[a,b]	0.9976	0.045	0.55∓0.I4
C	H_2O-MeCN	0.I6I∓0.0I2	I.000∓0.024	0.932∓0.026	-0.507∓0.05I	I2[c]	0.9994	0.022	I.97∓0.02
C-a		0.I7I∓0.0I6	I.806∓0.056	0.929∓0.033	-0.9I0∓0.II9	I2[a]	0.9990	0.028	I.98∓0.06
D	H_2O-An	0.I6I∓0.009	0.999∓0.022	0.940∓0.0I8	-I.252∓0.042	I0[c,e]	0.9998	0.0I5	0.80∓0.02
E	H_2O	0.I5I∓0.0I3	---	0.947∓0.037	---	7[f],	0.9992[h]	0.033[h]	---

[a]The measure S' of a solvent effect is derived as follows: S'_j = log k(p-NO_2, j-th mixture) - - log k(p-NO_2, H_2O). [b]For the rate constants in water, 50, 70, and in 80% mixtures. [c]The measure S' is derived as follows: S'_j = log k(H, j-th mixture) - log k(H,H_2O). [d]Without the log k values in 80% aqueous dioxane which do not deviate significantly from the preceding regression. [e]Significantly deviated point for m-NO_2-PA in 6I.6% acetone is excluded. [f]This regression is listed for a comparision; See Table 2. [h]Correlation coefficient (r) and the regression standard (s_0), respectively(See Table 2). The corresponding regression from Ref.2 and this one differ slightly, since they are based on different scales of constants $\hat{\sigma}^o$. [k]It is estimated as $\hat{\sigma}^o = -a_I/a_3$; and $s(\hat{\sigma}^o) \simeq s(a_I)$.

sions, b_0 and b_2 are equal to the estimates of log k_0 and ρ in equation (4) for PA's in water solution (See Reg.F and Table 2). Coefficient b_3 in Regs. A-a, B-a, and C-a, as well as in Regs. B, C, and D depends strongly, unlike a_3 in the similar equation[3] for EB's, on an organic component in the solvent system. In the case of EB's, the same isoparametric value was found for mixtures of water with EtOH, dioxane, acetone, and sulfolane, i.e. the linear regressions related to the equations similar to (4) and (5) tend to cross in the same point. However, there is no general equation (3) and, as a result, the general isoparametric value $\hat{\sigma}^0$ for hydrolysis of PA's in the solvent systems studied. Hence, for alkaline hydrolysis of PA's there is no linear relationship, valid for all solvent systems studied, between ρ in Eq. (4) and the corresponding parameters S' as well as there is no relationship (5) for any two PA's in all solvent mixtures as a whole (See Fig. 4 and Cf. with Fig.2 in Ref.3). There is also no linear

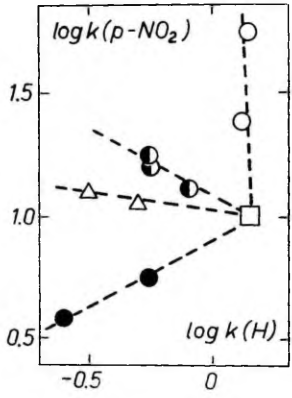


Fig.4. The lack of a generalized correlation (Cf. with Fig. 2 in Ref.3) between log k for p-NO_2-PA and for unsubstituted PA in water solution and in the binary systems investigated. The points □ , ○ , ◐ , △, and ● correspond to the hydrolysis in water solution, aq.EtOH, aq.dioxane, aq. acetone, and in aq. acetonitrile, respectively.

relationship, valid for all binary systems considered, between coefficient c_I in equation (5) and constant $\bar{\sigma}^0$ for the substituent in PA. Such relationships were found[3] in alkaline hyd-

rolysis of EB's. To account for the differences observed in combined effects of solvent and structural factors on alkaline hydrolysis of PA's and EB's one can assume that the features found for PA's are general for alkaline hydrolysis of the esters with structural variations in their leaving groups. On the other hand, the "splitting" in the isoparametric points, i.e. the differences in b_3, may be also related to the aroxy leaving group of PA's and one might find no such "splittings" for other leaving groups, e.g. for alkoxy groups. Both these hypotheses need special experimental examination.

Interpretations of IPP.

A. A Thermodynamic Approach. According to Ref.II, a change in activation free energy $\Delta\Delta G^{\neq}$ related to transfer of a reaction from solvent I to solvent 2, e.g. from water solution to some organo-aqueous mixture, equals the difference[+]

$$\Delta\Delta G^{\neq} = -2.3RT\log(k_2/k_I) = -2.3RT\,\delta_M \log k = \\ = \Delta G_t^o(Tr) - \Delta G_t^o(Rts) \qquad (7)$$

in the free energies of transfer of the transition state, $\Delta G_t^o(Tr)$, of the reaction and its reactants, $\Delta G_t^o(Rts)$, from solvent I to solvent 2. This is true, when both the reactants and the transition state are in thermal and quasi-chemical equilibria.

Three types of relation are possible between $\Delta G_t^o(Tr)$ and $\Delta G_t^o(Rts)$. They are (See Fig.5):

(a). $\Delta G_t^o(Tr) > \Delta G_t^o(Rts)$; it is equivalent to an inequality $\log k_2 < \log k_I$, i.e. change in a solvent decreases a rate constant (See Fig.5,a);

(b). $\Delta G_t^o(Tr) = \Delta G_t^o(Rts)$; in this case $\log k_2 = \log k_I$, i.e. the rate constant does not depend on a solvent (See Fig.5,b);

[+]The measures S_j and S_j' are linearly related to a change in activation energy of alkaline hydrolysis of esters when it is transferred from water solution to an organo-aqueous mixture of j-th composition; $S_j(S_j') = -\delta\Delta G_j^{\neq}/2.3RT$.

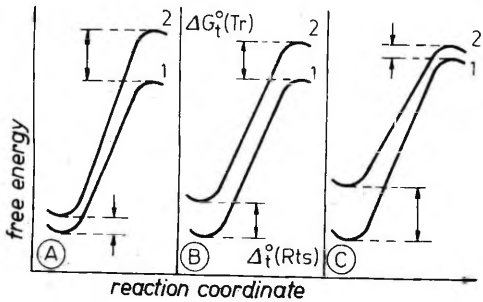


Fig.5. A thermodynamic interpretation of IPP within the framework of Eq.(7).Curves I and 2 are the free energy changes for a reaction in solvents I and 2. (a). A reaction slows down with transfer from solvent I to solvent 2 ($\bar{\sigma}^\circ < \hat{\bar{\sigma}}^\circ$), since $\Delta G_t^\circ(\mathrm{Rts}) < \Delta G_t^\circ(\mathrm{Tr})$; (b) A raaction is independent of a solvent ($\bar{\sigma}^\circ = \hat{\bar{\sigma}}^\circ$), since $\Delta G_t^\circ(\mathrm{Rts}) = \Delta G_t^\circ(\mathrm{Tr})$, and (c). A reaction accelerates with transfer to solvent 2 ($\bar{\sigma}^\circ > \hat{\bar{\sigma}}^\circ$) since $\Delta G_t^\circ(\mathrm{Rts}) > \Delta G_t^\circ(\mathrm{Tr})$. The relations between $\Delta G_t^\circ(\mathrm{Tr})$ and $\Delta G_t^\circ(\mathrm{Rts})$ do not depend on a mutual arrangements of curves I and 2.

(c). $\Delta G_t^\circ(\mathrm{Tr}) < \Delta G_t^\circ(\mathrm{Rts})$; it is equivalent to an inequality $\log k_2 > \log k_1$, i.e. a change in a solvent increases the rate constant (See Fig. 5, c).

In the alkaline hydrolysis of the esters,the free energy changes $\Delta G_t^\circ(\mathrm{Tr})$ and $\Delta G_t^\circ(\mathrm{Rts})$ and the relationship between them depend on a substituent. Hence a variation in the substituent structure may alter the relationship.Indeed,in the hydrolysis of PA's IPP ($\delta_M \log k = 0$) arises for some substituent,when the relationship (b) takes place for the corresponding ester,i.e. when the free activation energies for the reaction are equal in two (or more)solvents.For that substituent, $\bar{\sigma}^\circ = \hat{\bar{\sigma}}^\circ$. The relation (a) should take place for

all substituents whose effect on reactivity is smaller than the corresponding isoparametric one, i.e. when $\sigma < \hat{\sigma}$ as it is in EB's[3] in the binary systems considered, except aq. DMSO, or in the reaction for PA's with $\bar{\sigma}^{o} < \hat{\bar{\sigma}}^{o}$ in the corresponding solvent systems; see Fig. I. For such substituents, $\delta\Delta G^{\neq}$ or S' are controlled by a primary change, related to changes in a solvent, in free energy of the transition state. A relation (c) should be observed for the substituents whose effects on reactivities are greater than the corresponding isoparametric one, i.e. when $\sigma > \hat{\sigma}$ as in the hydrolysis of PA's with $\bar{\sigma}^{o} > \hat{\bar{\sigma}}^{o}$ in the solvents considered. In this case, $\delta\Delta G^{\neq}$ or S (S') are controlled by a primary change with changes in a solvent, in free energies of the reactants. Thus an increase in acceptor power of the leaving group substituent in PA leads to gradual transition from relation (a) to (b) and to (c). This is accompanied by a reverse of a solvent effect on rate constant of the reaction investigated.

B. Interpretation of IPP within the LFER Principle. According to equations (I) and (3), one can regard a total change in free energy of activation, $\Delta\Delta G^{o}_{tot}$, in alkaline hydrolyses of the esters as a sum of structural, $\Delta\Delta G^{o}_{st}$, and solvent, $\Delta\Delta G^{o}_{sol}$, terms

$$\Delta\Delta G^{o}_{tot} = \Delta\Delta G^{o}_{st} + \Delta\Delta G^{o}_{sol} \qquad (8)$$

In its turn, the term $\Delta\Delta G^{o}_{sol}$ consists of two oppositely varied contributions (See Table 4 and Ref.3). The first one depends on a substituent structure, while the other is structurally independent. In equations (I) and (3), the terms $a_I S$ ($b_I S'$) and $a_3\sigma$ ($b_3 S'\bar{\sigma}^{o}$) correspond to these contributions, respectively. One must keep in mind that $S < 0$ and $a_3 < 0$ for the hydrolysis of EB's, whereas in equation (3) both S' and b_3 are positive, when S' is evaluated from the data for PA whose substituent has $\bar{\sigma}^{o} > \hat{\bar{\sigma}}^{o}$ and negative in the opposite situation. IPP, i.e. independence of log k of a solvent mixture composition ($\Delta\Delta G^{o}_{sol} = 0$), should be observed for such substituent in the ester hydrolyzed that leads to equal but opposite in sign terms $b_I S'$ and $b_3 S'\bar{\sigma}^{o}$

(or $a_I S$ and $a_3 S\sigma$) in the corresponding equation for the reaction. For this substituent $\bar{\sigma}^o(\sigma) = \hat{\bar{\sigma}}^o(\hat{\sigma}) = -b_I/b_3$ ($-a_I/a_3$). For all substituents with $\bar{\sigma}^o(\sigma) > \hat{\bar{\sigma}}^o(\hat{\sigma})$ the structurally independent term (i.e. $-2.3RTa_I S$ or $-2.3RTb_I S'$) is controlled in $\Delta\Delta G^o_{sol}$ and it determines the dependence of log k on a solvent mixture composition. A similar situation should be observed in alkaline hydrolysis of EB's in mixtures of water with ethanol, dioxane, acetone, and sulfolane as well as in the hydrolysis of PA's in aq. acetonitrile. In alkaline hydrolysis of PA's in aqueous ethanol, dioxane or acetone, an increasing acceptor power of the leaving group substituent causes a gradual change in relation between two opposite contributions in $\Delta\Delta G^o_{sol}$. As a result of this change, a reverse of solvent effect on rate constant is observed, when group with $\bar{\sigma}^o < \hat{\bar{\sigma}}^o$ is substituted by a group with $\bar{\sigma}^o > \hat{\bar{\sigma}}^o$.

In spite of the differences observed in the combined effects of a solvent and structural changes on alkaline hydrolyses of PA's and EB's, there is an excellent correlation between the coefficients ρ^{PA} and ρ^{EB} in Hammett-Taft and Hammett equations found for two reactions in the same mixtures (See Fig.6). This relationship crosses the origin of coordinates

$$\rho^{PA} = (0.620 \mp 0.004)\rho^{EB} \qquad (9)$$
$$n = 4 \quad r = 0.9999 \quad s_0 = 0.019$$

The effects of acyl substituents and the leaving groups are rather independent[21-23] in the alkaline hydrolysis of the esters of carbon acids. Hence an intercept of regression (9) is a factor z_0 of transmission of an effect of the substituent Ar in an aroxy leaving group through the ethereal oxygen. This factor is evidently independent of a solvent.

The neccesary and sufficient condition, within equations (I) and (3) for hydrolyses of EB's and PA's, for relationship (9) should be a linear dependence between $a_3 S^{EB}$ and $b_3 S^{PA}$ in all binary systems obeying regression

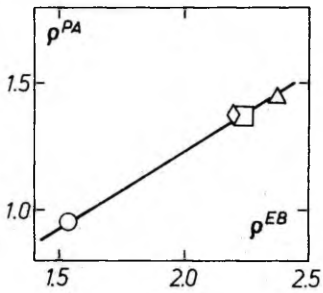


Fig.6. Linear relationship between the coefficients ρ of Hammett-Taft and Hammett equations for alkaline hydrolyses of PA's and EB's in water solution (○), 50% aq. EtOH (◇), 50% aq. dioxane (□), and in 61.6% aq. acetone (△).

Table 5

Coefficients and Statistics of Equations (10) and (11) for Alkaline Hydrolysis of PA's[a]

Eq.	b_0	b_I	b_2	$d(z_0)$	n	R	S_0
(10)	0.145∓ 0.010	0.937∓ 0.054	0.980∓ 0.047	-0.369∓ 0.049	20	0.9970	0.045
(11)	0.152∓ 0.005	0.973∓ 0.032	---	0.621∓ 0.007	19[b]	0.9990	0.025

[a]For log k of PA's in water solution, in 50% aq. EtOH, in 50% aq. dioxane and in 61.6% aq. acetone (See Table I). The organic component content in a binary mixture is in molar per cents. Parameters S^{EB} and coefficients ρ^{EB} are from Ref.3. [b]log k for p-NO_2-PA in aq. acetone is excluded as a significant outlier.

(9)[+], i.e. a proportionality should be observed between the corresponding structural contributions (see above) in changes

[+]The parameters S^{PA} and S^{EB} are linearly related in every solvent system taken separately but there is no general linear relationship between them that is valid in all solvent systems as a whole.

of free energy of solvation $\Delta\Delta G^{o}_{sol}$ in two reactions.

Equations (3) and (9) show that all rate constants for alkaline hydrolysis of PA's in water solution and in its mixtures with ethanol, dioxane and in aq. acetone should follow the generalized equations

$$\log k = b_0 + b_I S^{PA} + b_2 \bar{\sigma}^{o} + d S^{EB} \bar{\sigma}^{o} \qquad (10)$$

and

$$\log k = b_0 + b_I S^{PA} + z_0 \rho^{EB} \bar{\sigma}^{o} \qquad (11)$$

where $d = z_0 a_z$, S^{PA} and S^{EB} are the corresponding solvent measures for EB's and PA's, parameters S^{EB} and coefficients ρ^{EB} are from Ref. 3. The corresponding regressions (See Table 5) have high statistical indices and their coefficients agree well with the corresponding theoretical values. Eqns. (10) and (11) assume that two (see above) terms of the solvation contribution $\Delta\Delta G^{o}_{sol}$ in a free energy change for alkaline hydrolysis of PA's depend as a whole in different ways on a solvent being rather proportional in every binary system taken separately.

References

1. Istomin B.I., Finkelstein B.L., Sukhorukov Yu.I and Donskikh V.I., This J., 14, 476 (1977)
2. Istomin B.I., Eliseeva G.D. & Finkelstein B.L., This J., 15, 511 (1978)
3. Istomin B.I., Bazhenov B.N., Eliseeva G.D. & Finkelstein B.L., This J., 16, 185 (1979)
4. Palm V.A., Fundamentals of Quantitative Theory of Organic Rections, 2nd Ed., "Khimiya", Leningrad, 1977
5. Leffler J.E. & Grunwald E., Rates and Equilibria of Organic Reactions, J.Wiley & Sons, N.Y., 1963
6. Palm V.A., & Istomin B.I., Reakts. sposobn. org. soedin., 6, 427 (1969)
7. Istomin B.I., Pivovarov S.A., Selivanov V.F., Gidaspov B.N. & Istomina S.N., This J., 12, 287 (1975)

8. Finkelstein B.L., Sukhorukov Yu.I., Pivovarov S.A., Donskhikh V.I. & Istomin B.I., This J., 13, 351 (1976)
9. Istomin B.I., Sukhorukov Yu.I., Sukhorukova N.A., & Finkelstein B.L., This J., 14, 460 (1977)
10. Istomin B.I., Palm V.A. & Nummert V.M., Reakts.sposobn. org.soedin., 10, 609 (1973)
11. Finkelstein B.L., Sukhorukov Yu.I. & Istomin B.I., This J., 14, 181 (1977)
12. Gordon A., & Ford R., Chemist's Companion, (Russian Translation), "MIR", Moscow, 1976; Waisberger A. et al., Organic Solvents (Russian Translation), "IL", ,Moscow, 1958
13. Draper N.R. & Smith H., Applied Regression Analysis, J.Wiley & Sons, 1966; Russian Translation, "Statistika", Moscow, 1973
14. Rate and Equlibrium Constants of Heterolytic Organic Reactions, Ed.by V.Palm, Vol.I, Part 2, VINITI, Moscow, 1975
15. Tommila E. & Hinshelwood C.N., J.Chem.Soc., 1801 (1938)
16. Evans C.G. & Thomas J.D.R., J.Chem.Soc., B, 1502 (1971)
17. Ryan J.J. & Humfrey A.A., J.Chem.Soc.,B, 842 (1966)
18. Maremäe V.M. & Palm V.A., Reakts.sposobn.org.soedin., 1, No. 2, 85 (1965)
19. Zhdanov Yu.A.& Minkin V.I., Correlation Analysis in Organic Chemistry, (in Russian), Rostov University, Rostov-na-Donu, 1966
20. Abraham M.H., Prog.Phys. Org. Chem., 11, 1-88 (1974)
21. Kirsch J.F., Clewell W. & Simon A., J.Org.Chem., 33, 127 (1968)
22. Hancock C.K. & Falls C.P., J.Am.Chem.Soc.,83, 4214 (1961)
23. Bogatkov S.V., Thesis, Moscow State University, Moscow, 1977; Bogatkov S.V., This J., 14, 159+ (1977)

+In accordance with Russian Edition of this journal.

Comparative Investigation of the Nucleophilic Substitution Reactions at Phosphoryl and Carbonyl Centers. Part 7. Independent Structural Effects of Acyl and Leaving Groups in Esters $R_IC(O)OR_2$ on Their Alkaline Hydrolysis

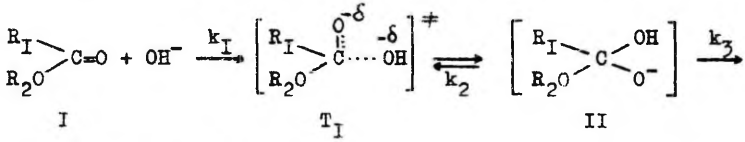
B.I.Istomin*, B.L.Finkelstein & G.D.Eliseeva

Petroleum Syntheses Institute at Irkutsk University, P.O. Box 1665, Irkutsk 664033

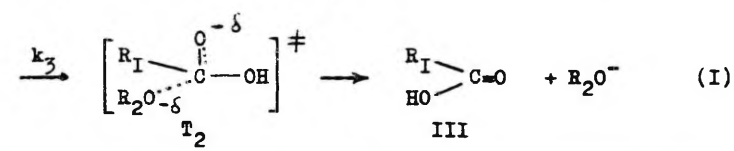
Received April 15, 1979

The analysis of the literature kinetic data for alkaline hydrolysis, in aqueous solution at 25°C, of esters $R_IC(O)OR_2$ with alkyl, electronegative aliphatic and with aromatic substituents R_I and R_2 reveals unambiguously that structural effects of these groups on the reaction rate constants are rather independent of each other. The "inner" measures are used for structural effects of R_I and R_2O. Within the framework of mechanism $B_{Ac}2$ for this reaction, the result obtained is in good agreement with the rate-limiting attack of anion OH^- on the ester carbonyl group.

Alkaline hydrolysis of esters $R_IC(O)OR_2$ is the most investigated reaction of nucleophilic substitution at the carbonyl carbon atom[1-7]. The reaction is believed[2,4,6,7] to have



I T_I II



T_2 III

(I)

a mechanism $B_{Ac}2$ related to a tetrahedral addition interme-

diate II and a rate-controlling step in this process appears to be an addition[4] of HO^-, i.e.

$$k_{obsd} = k_I \qquad (2)$$

As it is known[8-11], structural effects of both R_I and R_2 on log k_{obsd} for this reaction obey LFE relatioships accurately. According to Refs. 8 and 9 these groups affect additively the reaction rate constant, i.e. their structural effects appear to be independent in that reaction. However, this conclusion seems to be not very convincing, since it has been verified on a limited body of the experimental data. In the present paper we risk to solve more generally the problem of mutual effect of groups R_I and R_2 in alkaline hydrolysis of esters $R_IC(O)OR_2$. For this purpose we try and apply the polylinearity principle[12] (PPL) to as large body of the experimental data for the esters with alkyl, electronegative aliphatic, and aromatic groups R_I and R_2O and with R_I = H as possible.

The rate constants k_{obsd} for alkaline hydrolysis of esters $R_IC(O)OR_2$ in aqueous solution at 25° should obey, in accordance with PPL[12], the equation

$$\log k = a_0 + a_I X_I + a_2 X_2 + a_3 X_I X_2 \qquad (3)$$

if groups R_I and R_2 have non-additive effect on the free energy change in reaction (I). In this equation X_I and X_2 are the measures of structural effects of R_I and R_2 on the process, respectively. Taking arbitrary alkaline hydrolysis, in H_2O at 25°, of ethyl acetate as a standard process one can evaluate, in accordance with PPL, the scales X_I and X_2 in the following manner

$$X_I = \log k(R_IC(O)OEt) - \log k(MeC(O)OEt) \qquad (4)$$

$$X_2 = \log k(MeC(O)OR_2) - \log k(MeC(O)OEt) \qquad (5)$$

These "inner" scales place the following restraints[12] on the coefficients a_0 through a_2 in equation (2): a_0 = log k (MeC(O)OEt) = -0.96 (See Ref.5) and $a_I = a_2$ = I.00. The numerical values of X_I and X_2 for various R_I and R_2 are calculated by the experimental data of Ref. 5 and are listed

Table I

Coefficients and Statistics of Equation (3)[a]

Coefs. & Statcs.	Reg.I	Reg.2
a_0	-0.968∓0.002	-0.970∓0.002
a_I	I.002∓0.003	I.006∓0.002
a_2	I.0I5∓0.008	I.0I5∓0.009
a_3	0.025∓0.0I3	---
n^c	96[d]	96[d]
n^b	I05	I05
R	0.9996	0.9996
S_0	0.035	0.033

[a]In regression analysis we used the values of log k^{25}_{obsd} for esters $R_IC(0)OR_2$ with: R_2 = 2, R_I = I - 6, II, I3,I7 - I9,22, 23, 25,. 26,45-47; R_2 = 3, R_I = I-5,9,I4-I6; R_2 = 4, R_I = I-3, 5,II,22,23,26; R_2 = 5, R_I = I,3-5,22,23,26,27,34; R_2 =6, R_I = = I-5,22,23,26,27; R_2 = 7, R_I = 2; R_2 = I2, R_I = 2-5,22,23,26; R_2 = 28, R_I = 2,22,23,26; R_2 = 29, R_I = 2-5,22,23; R_2 = 30, R_I = 2-5,22,23,26; R_2 = 3I, R_I = 2-4,23; R_2 = 32, R_I = 2-5,22, 23,26; R_2 = 33, R_I = 2-5,22,23,26; R_2 = 34, R_I = 2,34; R_2 = 35, R_I = 2; R_2 = 38, R_I = 2; R_2 = 43, R_I = 2,34; R_2 = 44, R_I = = 2,34. The numeration of groups R_I and R_2 is the same as in Table 2. [b]Initial number of analyzed esters. [c]The number of points described by the regression found after exclusion of all significant outliers. [d]The points for esters $^-OC(0)(CH_2)_2C(0)OMe$, $PhCH_2C(0)OMe$, i-PrC(0)OPr-i, $HO(CH_3)_2CC(0)OPr$-i, $CH_3OCH_2C(0)OPr$-n, $CH_3OCH_2C(0)OPr$-i, PhC(0)OPr-i, $HOCH_2C(0)OPr$-i and HC(0)OPr-i.

in Table 2.With the presence[5] of a few log k values for the same ester which do not differ strongly,the corresponding mean values are used in all our considerations.

Table I lists the results of regression analysis, within equation (3), of log k^{25}_{obsd} values[5] for I05 esters. These es-

ters are combinations of 21 groups R_I and 18 groups R_2 from those listed in Table 2. It is noteworthy that only 25 ones of the analysing log k - values are used to evaluate X_I and X_2. In this Table Reg.I is practically adequate: $R > 0.999$ and $S_0 \simeq 0.03$ in log.units. Its coefficients a_0 through a_2 agree well with the corresponding theoretical values whereas a_3 is found to be insignificant. The cross-term exclusion (See Reg. 2) gives no biasings in the estimates for a_0, a_I, and a_2. Hence, coefficient a_3 is zero in fact. The regression 2 standard shows that its accuracy corresponds to an error within $\simeq 6\%$ of the log k value described. The log k values for $^{-}OC(O)(CH_2)_2C(O)OMe$ and $PhCH_2C(O)OMe$ as well as for i-PrC(O)OPr-i and $HO(CH_3)_2CC(O)OPr$-i are found to be the maximum ones of the significant outliers from Regs. I and 2. The deviations of two last points could be accounted for by assuming the lack of the additivity in the effects of α-branched groups R_I and R_2. This non-additivity might be related to additional steric interactions between such substituents. Confirmation for this hypothesis could be found in the following fact. The log k values for the esters with leaving groups i-PrO and $R_I = CH_3OCH_2$, Ph and $HOCH_2$ and H have small but significant deviations from Regs. I and 2. On the other hand, these regressions describe well the log k values for 23 other esters which have α-branched groups R_I and/or R_2. It is noteworthy, that esters i-PrC(O)OPr-i and $HO(CH_3)_2CC(O)OPr$-i have rather equal deviations from the regression surfaces. This fact is irrational within the above hypothesis. Hence, this hypothesis needs the special experimental testing. And we can conclude, within the present status quo in the experimental data for the process of interest, that various groups R_I and R_2 have independent structural effects[+] on alkaline hydrolysis rate constants for esters $R_IC(O)OR_2$. Fig. I illustrates the additivity of the substituent effects in the form of linear relationship of log k

[+]The rate constants with aryl groups R_I and R_2 which also are α-branched ones, follow accurately both Regs. I and 2; See also Ref.8.

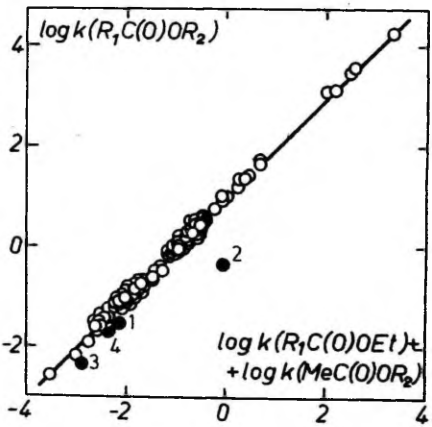


Fig. I. Independent structural effects of acyl (R_I) and leaving (R_2O) groups on alkaline hydrolysis of esters $R_IC(O)OR_2$: the plot of log $k^{25}(H_2O)$ for $R_IC(O)OR_2$ vs the sum of log $k^{25}(H_2O)$ values for the corresponding esters $R_IC(O)OEt$ and $MeC(O)OR_2$. Solid points correspond to the maximum outliers (See the text), i.e. $^-OC(O)(CH_2)_2C(O)OMe$ (I), $PhCH_2C(O)OMe$ (2), i-PrC(O)OPr-i (3) and to $HO(CH_3)_2CC(O)OPr$-i (4).

for esters $R_IC(O)OR_2$ vs. the sum of log k values for esters $R_IC(O)OEt$ and $MeC(O)OR_2$ with the same groups R_I and R_2. Eq.(3) is converted into this relationship, when $a_3 = 0$. As it is seen, the points for the most part of the esters with alkyl, electronegative, and aromatic groups R_I and R_2 yield accurately to the theoretical straight line whose slope and intercept should be equal to I.00 and - log k(MeC(O)Et)= = 0.96, respectively. Least squares treatment of the log $k(R_IC(O)OR_2)$ data as a function of the above sum leads to the regression equation

$$\log k(R_I C(O)OR_2) = (0.968 \mp 0.007) + (I.009 \mp 0.005)(\log k(R_I C(O)OMe) + \log k(MeC(O)OR_2)) \quad (6)$$

$$n = 96 \quad r = 0.9996 \quad s_0 = 0.046$$

Its intercept and slope are really equal to their theoretical values. From this regression points for the following esters (Cf. Table I) deviate significantly: $^{-}OC(O)(CH_2)_2C(O)OMe$, $PhCH_2C(O)OMe$, i-PrC(O)OPr-i, $HO(CH_3)_2CC(O)OPr$-i, $CH_3OCH_2C(O)OPr$-n, $MeOCH_2C(O)OPr$-i, PhC(O)OPr-i, $HOCH_2C(O)OPr$-i and HC(O)OPr-i. However, the large deviations are observed only for the four former ones of these esters (See Fig. I).

The above results force us to put forward the hypothesis that the detailed mechamism of alkaline hydrolysis is the same, in aqueous solution at any rate, for all esters which are described by the regression found. The lack of a statistically significant term of interaction between the acyl and leaving ; group substituents in the free energy change in the reaction may be related to approximate equality of the corresponding terms in the free energies for an initial and transition states in the rate-controlling step of the reaction. On the other hand, one might assume a lack of such interactions in both these states. The last assumption is unlikely, since various energy characteristics and properties of organic compounds are found to be non-additive[12,13]. It is easy to assume, on the other hand, that the terms related to interactions between R_I and R_2 are equal in the initial state I (See scheme(I)) and in the transition state T_I, since formation of the new $C(O)\cdots\cdots OH^{-}$ bond is related to simultaneous π-bond breaking in the carbonyl group and should not perturb the interactions between groups R_I and R_2 to an observable extent.This interpretation assumes, in accordance with Ref. 4,that the rate-controlling step of the reaction is an attack of anion OH^{-}.Assuming a decomposition of intermediate II as a rate-determining step in the reaction,one should also assume such transition state unsimilar to T_2 between states II

and III in which the interactions of R_I and R_2 will be approximately equal to those in intermediate II. It is very difficult to imagine such a transition state, since elimination of the leaving group from the intermediate molecule should be preceded by weakening its bond with the reaction center in this transition state. This weakening will lead to a different interaction terms in the free energies of this transition state and intermediate II. As a result of this difference we might observe a statistically significant cross-term in Equation (3).

It is noteworthy that deviations observed for some esters with α-branched groups R_I and R_2 do not apparently prove that all effects of these groups on alkaline hydrolysis of the esters $R_IC(O)OR_2$ may be non-additive. The steric interactions seem to be non-additive[12,13] as a whole and this non-additivity might hide to a some extent the actual additivities in the electronic effects of the groups R_I and R_2. Hence, intending to check more thoroughly the character of the combined effect of these groups in alkaline hydrolysis of the esters $R_IC(O)OR_2$ one should analyze only those esters whose groups R_I as well as groups R_2 are isosteric and differ in their abilities to inductive and resonance interactions. This way was used successfully in Ref.8 that showed unambiguously an additivity in the effects of acyl and leaving group substituents on alkaline hydrolysis of the esters $ArC(O)OAr$.

Refs. 9 show an additivity in the effects of groups R_I and R_2 on alkaline hydrolysis of some esters in aqueous solution and in aqueous ethanol. Ref.8 reveals this in aqueous acetonitlile. We find here the same behaviour in aqueous solution. Thus one can generalize that an additivity in the effects of those groups on alkaline hydrolysis of the esters $R_IC(O)OR_2$ does not depend on a solvent, i.e. on organic component in solvent mixture.

If tetrahedral intermediate formation is the rate-controlling step in the reaction considered, then, in accordance with scheme (I), substituents R_I and OR_2 should

be equivalent[+] in their effects on reactivity of the carbonyl group of the ester molecule in its reaction with OH^-. Thus, one may expect rather large similarities in the structural effects on the reaction of present interest and on the reaction of HO^- addition to ketones and aldehydes as it has been found for the hydration equilibria for ketones, aldehydes and for amides.

An argument for the idea that groups R_I and R_2O have the same polar effects on alkaline hydrolysis of $R_IC(O)OR_2$ one might find in the ratio of coefficients ρ in Hammett-Taft equations for the hydrolyses of phenyl acetates[I7] and bis-m,p-substituted aryl carbonates[I8] ArOC(O)OAr in 50%(v/v) aqueous dioxane. For the first series we found[I7] ρ^{PA} = = 1.353±0.067 at 25°. For the latter series[++], the Hammett-Taft equation should be as follows

$$\log k(ArOC(O)OAr) = \log k(PhOC(O)OPh) + (\rho_I + \rho_2)\bar{\sigma}^{\circ} \qquad (7)$$

Here ρ_I and ρ_2 are susceptibilities of the reaction to the electronic effects of the leaving and remaining aroxy groups, respectively. According to the above idea, the coefficients

[+]That is, the reaction should have the same or approximately the same susceptibilities to polar effects of groups R_I and OR_2 (i.e. $\rho^*(R_I) \cong \rho^*(R_2O)$), to their steric effects ($\delta(R_I) \cong \delta(R_2O)$) and to their resonance effects as well as it has been found[I4] for effects of substituents X_I and X_2 on dissociation ot acids $X_IX_2P(O)OH$.

[++]The rate measurements for this reaction are believed[I8] to be related to an elimination of the first aroxy group from a carbonate molecule. The second group eliminates with unmeasureably large rate from the unstable monoester anion.

Table 2

The Measures X_I and X_2 of Structural Effects of Substituents R_I and R_2 on Alkaline Hydrolysis of Esters $R_IC(O)OR_2$

No.	Substituent	X_I^a	X_2^b	No.	Substituent	X_I^a	X_2^b
I	H	2.37		25	CH_2NH_2	0.77	
2	Me	0.00	0.22	26	$CH(OH)CH_3$	0.95	
3	Et	-0.07	0.00	27	$C(CH_3)_2OH$	-0.03	
4	n-Pr	-0.32	-0.05	28	$(CH_2)_2Cl$		0.52
5	i-Pr	-0.43	-0.64	29	$(CH_2)_2OCH_3$		0.28
6	n-Bu	-0.35	-0.I0	30	$(CH_2)_2OC_2H_5$		0.27
7	i-Bu	-0.9I	-0.I4[c]	3I	$(CH_2)_2OC_4H_9$		0.25
8	s-Bu		-0.76[c]	32	$(CH_2)_3Cl$		0.I9
9	t-Bu	-I.62	-I.78	33	$(CH_2)_3OCH_3$		0.06
I0	Am		-0.I5	34	Ph	-0.52	I.I2
II	tr-CH=CHCH$_3$	-0.93		35	p-MeØ	-0.73	I.02
I2	$CH_2CH=CH_2$		-0.I9	36	m-MeØ		I.03
I3	$COCH_3$	3.86		37	m-ClØ	0.05	
I4	CH_2F	2.I5		38	p-ClØ	-0.I9	I.30
I5	CHF_2	4.43		39	p-BrØ	-0.I6	I.39
I6	CF_3	5.22		40	p-MeOØ	-0.96	I.05
I7	CH_2Cl	2.38		4I	m-NH_2Ø	-0.62	
I8	$CHCl_2$	3.69		42	p-NH_2Ø	-I.54	I.5I
I9	CCl_3	4.26		43	m-NO_2Ø	0.56	I.86
20	CH_2Br	2.50		44	p-NO_2Ø	0.64	I.96
2I	$CHBr_2$	3.27		45	$(CH_2)_2COO^-$	-0.46	
22	CH_2OH	I.03		46	CH_2COO^-	-0.76	
23	CH_2OCH_3	I.I2	0.66	47	$PhCH_2$	0.40	
24	$CH_2COOC_2H_5$	I.29					

[a]Those values are calculated by Equation (4) from the data compilled in Ref.5. [b]These values are calculated by equation (5) from the data of Ref.5. [c]The value of log k^{25} is calculated by Arrhenius relationship based on the data of Ref.5 measured at other temperatures.

ρ_I and ρ_2 should be equal to each other. These values should also equal ρ^{PA}, since the effects of R_I and R_2O on the reaction considered are rather independent. Actually we find for alkaline hydrolysis of the carbonates[18] at 20°+ the correlation

$$\log k(ArOC(O)OAr) = (-0.070\pm0.06I) + (2.784\pm0.I8I)\bar{\sigma}^{o} \quad (8)$$
$$n = I0 \quad r = 0.9834 \quad s_0 = 0.I63$$

Its slope is twice as high as that for phenyl acetates, i.e. $\rho(ArOC(O)OAr)/\rho^{PA} = 2$. This result confirms strongly that ρ_I and ρ_2 in equation (7) are really equal. The more thorough check of the hypothesis of equal polar effects of groups R_I and R_2O on alkaline hydrolysis of the esters one might do on the basis of esters $ArCH_2C(O)OAr$ whose groups R_I and R_2O are isosteric. This series, however, is not studied experimentally as we can see that from the recent compilation[5].

R e f e r e n c e s

I. Ingold C., Structure and Mechanism in Organic Chemistry, Cornell University Press, I969; Russian Translation, "Mir", Moscow, I973, Chap. I5.

2. Becker H.G.O., Einführung in die Electronentheorie organisch-chemischer Reaktionen, VEB Deutscher Verlag der Wissenschaften, Berlin, I974; Russian Translation, "Mir", I977, Chap.6

3. Gould E.S., Mechanism and Structure in Organic Chemistry, Chap.9 , Holt, Rinechart & Wistan, New York, I959

4. Ritchie C., J.Am.Chem.Soc., 97, II70 (I975)

5. Tables of Rate and Equilibria Constants for Heterolytic Organic Reactions, Vol.I, Part 2, Ed.by V.Palm, VINITI, Moscow, I975

6. Jencks W.P., Catalysis in Chemistry and Enzymology, McGraw-Hill Book Co., I969; Russian Translation, "Mir", Moscow, I972

+The numerical magnitude of ρ^{PA} is practically independent of temperature.[19]

7. Isaacs N.S., Reactive Intermediates in Organic Chemistry, Chap.8, J.Wiley & Sons, I974
8. Kirsch J.F., Clewell W., & Simon A., J.Org.Chem., 33, I27 (I968)
9. Bogatkov S.V., This J., I4, I59 (I977); Babaeva L.G., Bogatkov S.V., Kruglikova R.I. & Unkovski B.V., This J., II, 56I (I974); Bogatkov S.V., Thesis, Fine Chemical Technology Institute, Moscow, I977
I0. Taft R.W., Chap.I3 in Book "Steric Effects in Organic Chemistry", Ed.by Newman, J.Wiley & Sons; Russian Translation, IL Publs., Moscow I960; Jaffe H.H., Chem.Revs., 53, I9I (I953); Hammett L.P., Physical Organic Chemistry, McGraw-Hill Book Co., N.Y., I940
II. Püssa T.O., Thesis, Tartu State University, Tartu, I973
I2. Palm V.A., Fundamentals of Quantitative Theory of Organic Reactions (in Russian), "Khimiya", Leningrad, I977; Rudakov E.S., Doklady akademii nauk SSSR, 24I, 635 (I978)
I3. Istomin B.I., & Palm V.A., Reakts. sposobn. org.soed., 8, 833, 845 (I97I); 9, 433, 469, 847, I089, II05, I225 (I972); I0, 537, 567, 583 (I973); Istomin B.I., Thesis, Tartu State University, Tartu, I973
I4. Istomin B.I.,& Baransky V.A., This J., I2, 69 (I975); I5, 23I, 284, 299 (I978)
I5. Fastrez J., J.Am.Chem.Soc., 99, 7004 (I977)
I6. Draper N.R. & Smith H., Applied Regression Analysis, J.Wiley & Sons, I966; Russian Translation, "Statistika" Moscow, 1973
I7. Istomin B.I., Bazhenov B.N., Eliseeva G.D. & Finkelstein B.L., This J., I6, I96 (I979)
I8. Cooper G.D., Johnston H.T.,& Williams B., J.Org.Chem., 30, 3889 (I965); Cooper G.D. & Williams B., J.Org.Chem., 27, 37I7 (I962)
I9. Istomin B.I., Eliseeva G.D. & Finkelstein B.L., I5, 5II (I978)

Methanolysis Kinetics of o.o- Dimethylchlorothiophosphate

A.Ph.Vasilyev and N.M.Loznikova

All-Union Scientific-Reseach Institute of Plant Protection Chemicals, Moscow

Received April 25, 1979

On the example of the dimethylchlorthiophosphate reaction the advantages of the parametric expansion of the free activation energy into additive mole fractions of the reaction mixture components to describe the kinetics of chemical processes in the liquid homogeneous phases without solvents or in the concentrated solutions have been shown. The application of such an expansion provides a means for describing the reaction kinetics with a few parameters. The constants of such an expansion have a distinct thermodynamic meaning: the linear coefficients correspond to the logarithms of the rate constants in an excess of the corresponding components.

It is practically impossible, except for few cases, to determine the reaction rate equation as a function of all factors and variables with the use of concentrated initial compounds[1], because in the concentrated solutions or in the liquid homogeneous media without solvents (unlike the reaction in dilute solutions or gas phase) the interaction of the reaction substances is complicated both by solvent effects (specific and non-specific solvation) and combined influence of other moleculs. The investigation of such processes is also complicated by the necessity to quantitatively estimate the total solvent effect.

In the previous report[2] we wrote that the methanolysis of dimethylchlorothiophosphate at low degree of conversion can

be successfully described by the third-order kinetic equation (for determination of the reaction rate constants we carried out experiment with the following initial mole ratios: $PSCl_3$: CH_3OH from 1:100 to 1:300 at temperatures -45° ÷ -15°C ; $(CH_3O)P(S)Cl_2$:CH_3OH from 1:2 to 1:4 at temperatures -15° ÷ 50°C and $(CH_3O)_2P(S)Cl$:CH_3OH from 2:1 to 1:20 at temperatures 25° ÷ 50°C). In the present work the more detailed investigation of dimethylchlorothiophosphate methanolysis will be begun with the simple reaction not complicated by consecutive ones. We have used the reaction of dimethylchlorothiophosphate with methyl alcohol as an example.

Experimental

Absolute methyl alcohol was obtained according to Ref.[3] and the solutions of hydrogen chloride in methanol - according to Ref.[4]. Experimentation, synthesis, and purification of dimethylchlorothiophosphate are described in Ref.2.

The formulae for calculating the reaction rate (by the decrease in dimethylchlorothiophosphate concentration), the reaction mixture volume, the running concentrations of dimethylchlorothiophosphate, trimethylthiophosphate, methanol and hydrogen chloride are as follows:

$$V = \frac{a}{100} \cdot [g_2(\tau_0)/d_2 + g_3(\tau_0)] + b/d,$$

$$n_{alc.}(\tau_i) = n_{alc.}(\tau_0) - 2[n_2(\tau_0) - n_2(\tau_i)] - n_{HCl}(\tau_0) \qquad (1)$$

$$n_{HCl}(\tau_i) = n_{HCl}(\tau_0) + n_2(\tau_0) - n_2(\tau_i),$$

$$C_{alc.}(\tau_i) = n_{alc.}(\tau_i)/V,$$

$$C_{HCl}(\tau_i) = n_{HCl}(\tau_i)/V,$$

$$C_{alc.}(\tau_0) = [n_{alc.}(\tau_0) - n_{HCl}(\tau_0)]/V,$$

$$C_{HCl}(\tau_0) = n_{HCl}(\tau_0)/V,$$

$$C_2(\tau_i) = n_2(\tau_i)/V,$$

$$C_3(\tau_i) = [n_2(\tau_0) - n_2(\tau_i)]/V,$$

$$C_2(\tau_0) = n_2(\tau_0)/V,$$

$$\varphi_2(\tau_i) = [C_2(\tau_{i+1}) - C_2(\tau_{i-1})]/(\tau_{i+1} - \tau_{i-1})$$

where $\mathcal{V}_2(\tau_i)$ is the reaction rate (in mol./l.·hr) at the moment τ_i;

V is the volume of the reaction mixture (in l.);

a is the weight (in g) of dimethylchlorothiophosphate;

$g_2(\tau_0)$ and $g_3(\tau_0)$ are the amounts (w/w) of dimethylchlorothiophosphate and trimethylthiophosphate in initial weight portion, respectively;

d_2 and d_3 are the specific weights (in g/l.) of dimethylchlorothiophosphate and trimethylthiophosphate, respectively;

b and d are the weight (in g) and the specific weight (in g/l.) of methyl alcohol or solution of hydrogen chloride in methanol, respectively;

$n_2(\tau_0)$, $n_{alc.}(\tau_0)$, and $n_{HCl}(\tau_0)$ are mole quantities of dimethylchlorothiophosphate, methanol, and hydrogen chloride at the initial moment of the reaction (τ_0), respectively;

$C_2(\tau_0)$, $C_{alc.}(\tau_0)$, and $C_{HCl}(\tau_0)$ are the concentrations (in mol./l.) of dimethylchlorothiophosphate, methanol, and hydrogen chloride at the initial moment of the reaction (τ_0), respectively;

$n_2(\tau_i)$, $n_{alc.}(\tau_i)$, and $n_{HCl}(\tau_i)$ are the mole quantities of dimethylchlorothiophosphate, methanol, and hydrogen chloride at the moment τ_i, respectively;

$C_2(\tau_i)$, $C_3(\tau_i)$, $C_{alc.}(\tau_i)$, and $C_{HCl}(\tau_i)$ are the concentrations (in mol./l.) of dimethylchlorothiophosphate, trimethylthiophosphate, methanol, and hydrogen chloride at the moment τ_i, respectively.

In this work to calculate instantaneous rate constants the "smoothed"[5] running values were used for all reaction mixture component concentrations and for instantaneous rates $\mathcal{V}_2$:

$$C(\tau_i)=\frac{1}{35}\cdot[-3C(\tau_{i-2}) + 12C(\tau_{i-1}) + 17C(\tau_i) + 12C(\tau_{i+1}) - 3C(\tau_{i+2})], \quad (2)$$

$$\mathcal{V}_2(\tau_i) = \frac{1}{10}\cdot[-2C_2(\tau_{i-2}) - C_2(\tau_{i-1}) + C_2(\tau_{i+1}) + 2C_2(\tau_{i+2})], \quad (3)$$

$$\mathcal{V}_2(\tau_i) = -k_2(\tau_i)\cdot C_2(\tau_i)\cdot[C_{alc.}(\tau_i)]^2, \quad (4)$$

$$\mathcal{V}_2(\tau_i) = -k_{2-II}(\tau_i)\cdot C_2(\tau_i)\cdot C_{alc.}(\tau_i), \quad (5)$$

where $k_2(\tau_i)$ and $k_{2-\text{I}}(\tau_i)$ are the observed third- and second-order rate constants, respectively.

The parameters of equations (8), (10), (11), (12), and (13) have been found by the least-squares method on a Nicolet BNC 12 computer by specially composed programms.

Results and Discussion

According to Table 1 the observed third-order rate constants $k_2(\tau_i)$ calculated by equation (4) keep constancy during every experiment satisfactorily (up to 80% degree of conversion), but they depend on the initial mole proportions of the reacting compounds. The dependence of the logarithms of the observed third-order rate constants, lg k_2, on the dimethylchlorthiophosphate mole fraction $N_2(\tau_0)$ is illustrated in Figure 1. In Figure 1 one can also see the plot of the logarithms of the observed second-order rate constants lg $k_{2-\text{I}}$ ($k_{2-\text{I}}$ were calculated by equation (5)) vs. $N_2(\tau_0)$. The numbers of points in Figure 1 correspond to those of experiments in Table 1.

The interaction between dimethylchlorthiophosphate and solutions of hydrogen chloride in methanol is also satisfactorily described by equations (4), (6) (see Table 1), and (5):

$$w_2(\tau_i) = -k_2(\tau_i)\cdot C_2(\tau_i)\cdot C_{alc.}(\tau_i)\cdot [C_{HCl}(\tau_i)]^{-1}. \qquad (6)$$

The observed third- and second-order rate constants are satisfactorily constant during every experiment. Besides, the observed rate constants decrease with increase in the hydrogen chloride mole fraction $N_{HCl}(\tau_0)$, if the initial mole proportions of dimethylchlorothiophosphate $N_2(\tau_0)$ and methanol $N_{alc.}(\tau_0)$ are constant.

As is known, with hydrogen chloride being solved in methanol the following reaction occurs:

$$HCl + CH_3OH \rightleftharpoons CH_3OH_2^+Cl^-, \qquad (7)$$

where the equilibrium is essentially shifted to the right[6]. Hydrogen chloride reacts with methanol to form methyl chloride and water[4,6-15], changes in the hydrogen chloride concentration changing the rate constants of the direct and backward

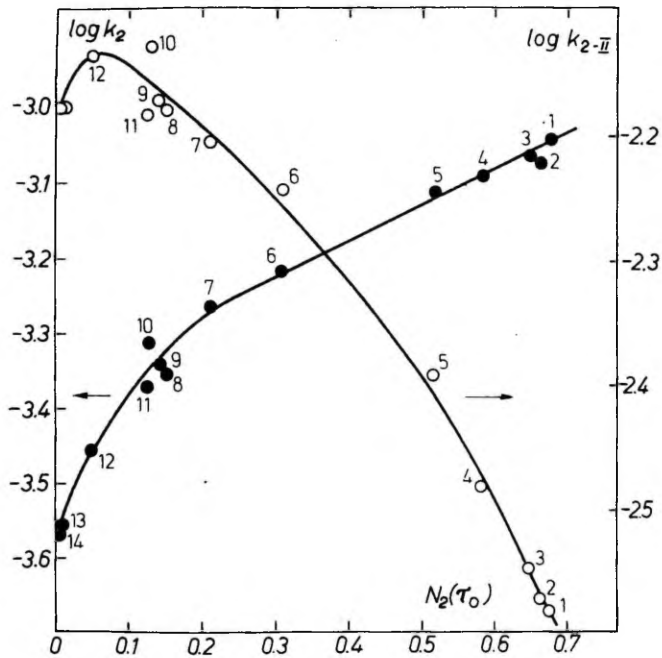


Fig.1. Plot of the logarithms of the third-order (lg k_2 - •) and the second-order (lg k_{2-II} - ○) rate constants vs. the dimethylchlorothiophosphate mole fraction $N_2(\tau_0)$

reactions with increase in the conversion degree[4,8].

When studying the reaction kinetics of dimethylchlorothiophosphate with methanol the formation of a small amount of methyl chloride was observed at high temperatures enough (50°C) and also for the reaction of dimethylchlorothiophosphate with solutions of hydrogen chloride in methanol. We assume that changes in methanol concentrations in reaction (7) or in side reactions are taken into consideration when calculating the instantaneous concentrations of free methanol by equation (1). Besides, in our estimation the rate constants of the re-

Table 1

No. of Expt.	τ_i [hr]	$k_2(\tau_i)\cdot10^4$ [l²/mol².·hr] calc. by Eq.(4)	No. of Expt.	τ_i [hr]	$k_2(\tau_i)\cdot10^4$ [l²/mol².·hr] calc. by Eq. (4)	No. of Expt.	τ_i [hr]	$k_2(\tau_i)\cdot10^4$ [l²/mol².·hr] calc. by Eq.(4)	No. of Expt.	τ_i [hr]	$k_2(\tau_i)\cdot10^4$ [l²/mol².·hr] calc. by Eq.(4)	No. of Expt.	τ_i [hr]	$k_2(\tau_i)\cdot10^4$ [l²/mol².·hr] calc. by Eq.(4)	$k(\tau_i)\cdot10^2$ [l./mol.·hr] calc. by Eq.(6)
1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	4
1	2	9.17	5	2	8.64	8	2	4.51	11	2	4.28	14	2	3.02	
	3	10.4		3	8.84		3	5.09		3	4.73		3	2.74	
	4	10.6		4	8.56		4	5.51		4	4.67		4	2.60	
	5	10.5		5	7.75		5	5.12		5	4.25		5	2.40	
	6	10.5		6	7.68		6	4.88		6	4.51		6	2.67	
	7	9.24		7	7.69		7	4.57		7	4.86		7	2.80	
	8	7.90		8	6.44		8	4.84					8	2.73	
	9	7.69		9	6.16		9	4.91	12	1	2.96				
										1.5	3.26	15	2	3.61	0.76
2	2	8.73				9	2	4.57		2	3.43		3	3.68	0.77
	3	8.86	6	2	6.13		3	4.86		2.5	3.69		4	3.85	0.89
	4	8.45		3	6.27		4	4.82		3	3.76		5	3.58	0.88
	5	8.16		4	6.38		5	4.74		3.5	3.71		6	3.42	0.88
				5	6.30		6	4.56		4	3.64		7	3.76	1.01
3	2	8.25					7	4.78		4.5	3.58				
	3	9.08					8	4.72		5	3.72	16	2	2.45	0.86
	4	9.33	7	2	5.06		9	4.90					3	2.69	0.96
	5	9.01		3	5.39				13	2	2.82		4	2.67	0.96
	6	9.17		4	5.70	10	2	4.51		3	2.79		5	2.59	0.94
				5	5.91		3	4.85		4	2.85		6	2.38	0.87
4	2	8.95		6	5.51		4	5.13		5	2.93		7	2.22	0.82
	3	8.67		7	4.92		5	5.23		6	2.85		8	2.39	0.85
	4	8.07		8	4.17		6	5.22		7	2.84		9	2.41	0.89
							7	5.17							

Table 1 (continued)

1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
17	2	2.12	0.78	18	2	2.95	1.18	19	2	1.98	1.20	20	2	1.21	0.86	21	2	1.40	1.14
	3	2.18	0.81		3	2.93	1.20		3	1.94	1.18		3	1.30	0.92		3	1.55	1.11
	4	2.28	0.87		4	2.72	1.14		4	1.91	1.17		4	1.31	0.93		4	1.70	1.21
	5	2.22	0.86		5	2.36	1.01		5	2.07	1.26		5	1.38	0.98		5	1.73	1.24
	6	2.25	0.88		6	2.57	1.01		6	2.30	1.41		6	1.47	1.04		6	1.77	1.26
	7	2.23	0.88		7	2.88	1.26		7	2.09	1.28		7	1.44	1.02		7	1.72	1.22
	8	2.11	0.83																
	9	2.11	0.84																

In Table 1 the experimental numbers and the mole proportions $n_2(\tau_0):n_{alc.}(\tau_0):n_{HCl}(\tau_0)$ are:

1 - 1 : 0.47 : 0
2 - 1 : 0.51 : 0
3 - 1 : 0.54 : 0
4 - 1 : 0.71 : 0
5 - 1 : 0.93 : 0
6 - 1 : 2.25 : 0
7 - 1 : 3.77 : 0
8 - 1 : 5.60 : 0
9 - 1 : 6.10 : 0
10 - 1 : 6.75 : 0
11 - 1 : 6.91 : 0
12 - 1 : 20.3 : 0
13 - 1 : 107 : 0
14 - 1 : 362 : 0
15 - 1 : 7.32 : 0.34
16 - 1 : 3.69 : 0.94
17 - 1 : 4.45 : 1.02
18 - 1 : 7.11 : 1.17
19 - 1 : 7.26 : 2.72
20 - 1 : 7.09 : 7.28
21 - 1 : 7.88 : 8.60

action of hydrogen chloride with methyl alcohol at 25°C are about 1,5 ÷ 2 (in some cases about 1) orders of magnitude less than those of the reaction under study.

To describe the kinetics of the dimethylchlorothiophosphate methanolysis we have used equation (8)

$$-w_2(\tau_i) = K_a \cdot C_2(\tau_i) \cdot C_{alc.}(\tau_i) + K_b \cdot C_2(\tau_i) \cdot [C_{alc.}(\tau_i)]^2 + K_c \cdot C_2(\tau_i) \cdot C_{HCl}(\tau_i) + K_d \cdot C_2(\tau_i) \cdot [C_{HCl}(\tau_i)]^2 / C_{alc.}(\tau_i) - K_e \cdot C_3(\tau_i) \cdot C_{HCl}(\tau_i) + K_f \cdot C_2(\tau_i) \cdot C_{alc.}(\tau_i) \cdot C_{HCl}(\tau_i), \quad (8)$$

obtained from the following assumed scheme of the process (the formation of the complexes between dimethylchlorothiophosphate or trimethylthiophosphate and methanol by virtue of hydrogen bonds can be observed by changes in the O-H vibration intensity in the region of 3500 ÷ 3700 cm^{-1}):

$$(CH_3O)_2PSCl + CH_3OH \longrightarrow (CH_3O)_3PS + HCl$$

$$HCl + CH_3OH \rightleftharpoons [CH_3OH \cdot HCl]$$

$$(CH_3O)_2PSCl + CH_3OH \rightleftharpoons [(CH_3O)_2PSCl \cdot CH_3OH]$$

$$(CH_3O)_2PSCl + HCl \rightleftharpoons [(CH_3O)_2PSCl \cdot HCl]$$

$$(CH_3O)_2PSCl + [CH_3OH \cdot HCl] \longrightarrow (CH_3O)_3PS + 2HCl$$

$$[(CH_3O)_2PSCl \cdot HCl] + CH_3OH \longrightarrow [(CH_3O)_3PS \cdot HCl] + HCl$$

$$[(CH_3O)_2PSCl \cdot HCl] + [CH_3OH \cdot HCl] \longrightarrow [(CH_3O)_3PS \cdot HCl] + 2HCl$$

$$[(CH_3O)_2PSCl \cdot CH_3OH] + CH_3OH \longrightarrow (CH_3O)_3PS + [CH_3OH \cdot HCl]$$

$$[(CH_3O)_2PSCl \cdot CH_3OH] + [CH_3OH \cdot HCl] \longrightarrow [(CH_3O)_3PS \cdot CH_3OH] + 2HCl$$

$$(CH_3O)_3PS + CH_3OH \rightleftharpoons [(CH_3O)_3PS \cdot CH_3OH]$$

$$(CH_3O)_3PS + HCl \rightleftharpoons [(CH_3O)_3PS \cdot HCl]$$

$$[(CH_3O)_2PSCl \cdot CH_3OH] \longrightarrow (CH_3O)_3PS + HCl.$$

This chemical six-parameter model (i.e. equation (8)) describes the experimental data with the error less then 10% (maximum error is about 25%), but the rate constant K_c is negative and K_e (the rate constant of the back reaction) is positive that does not correspond to the meaning of the model used. By consecutive elimination of insignificant

coefficients one can obtain the model of a third-order reaction. However, it was noted earlier that in such a case the experimental data all could be described with small accuracy only. The further complication of this chemical model is not advisable, since for concentrated solutions the solvent effects must be of great importance.

To describe the experimental data we have used the Palm equation (9)[16,17]

$$\ln K = \sum_{i=1}^{n} N_i \cdot \ln K_i \qquad (9)$$

where K and K_i are the reaction rate constants in the mixture of the solvents and in the "i-solvent", respectively, N_i is the mole fraction of the "i-solvent".

In our case we interpreted N_i in the Palm equation (9) as mole fractions $N_i(\tau_i)$ of the reaction mixture components, that is we supposed that the reaction of dimethylchlorothiophosphate with methanol took place in the mixed solvent whose composition was changed with time:

$$\ln k_2(\tau_i) = N_2(\tau_i)\cdot\ln K_2 + N_{alc.}(\tau_i)\cdot\ln K_{alc.} + N_3(\tau_i)\cdot\ln K_3 + N_h(\tau_i)\cdot\ln K_h, \qquad (10)$$

where $k_2(\tau_i)$ is the observed third-order rate constant at the moment τ_i;

K_2, $K_{alc.}$, K_3, and K_h are the rate constants of the reaction of dimethylchlorothiophosphate with methanol in: dimethylchlorothiophosphate methanol, trimethylthiophosphate, and in a certain hypothetical solvent which consists of hydrogen chloride complexes with methanol (the "h-solvent"), respectively;

$N_2(\tau_i)$, $N_{alc.}(\tau_i)$, $N_3(\tau_i)$, and $N_h(\tau_i)$ are the mole fractions of dimethylchlorothiophosphate, methanol, trimethylthiophosphate and the "h-solvent", respectively (the mole fractions of compounds which may be obtained by side reactions are included into $N_h(\tau_i)$).

Equation (10) describes the experimental data satisfactorily, the maximum error was less than 22% (mean error was less than 15%).

Much better agreement between experimental and calculated values of $k_2(\tau_i)$ was observed with the use of a non-linear model (mean error is within 7%):

$$\ln k_2(\tau_i) = N_2(\tau_i)\cdot\ln K_2 + N_{alc.}(\tau_i)\cdot\ln K_{alc.} + N_3(\tau_i)\cdot\ln K_3 + N_h(\tau_i)\cdot\ln K_h + N_2(\tau_i)\cdot N_{alc.}(\tau_i)\cdot\ln K_{2\text{-}alc.} + N_2(\tau_i)\cdot N_3(\tau_i)\cdot\ln K_{2\text{-}3} + N_2(\tau_i)\cdot N_h(\tau_i)\cdot\ln K_{2\text{-}h} + N_{alc.}(\tau_i)\cdot N_3(\tau_i)\cdot\ln K_{alc.\text{-}3} + N_{alc.}(\tau_i)\cdot N_h(\tau_i)\cdot\ln K_{alc.\text{-}h} + N_3(\tau_i)\cdot N_h(\tau_i)\cdot\ln K_{3\text{-}h}, \quad (11)$$

where, however, the non-linear terms all (with the exception of $N_2(\tau_i)\cdot N_h(\tau_i)\cdot\ln K_{2\text{-}h}$) were statistically insignificant. The statistically reliable model (the mean error was less than 10%, the maximum one was about 15%) is as follows:

$$\ln k_2(\tau_i) = -4.439\cdot N_2(\tau_i) - 8.193\cdot N_{alc.}(\tau_i) - 2.499\cdot N_3(\tau_i) - 8.083\cdot N_h(\tau_i) - 32.30\cdot N_2(\tau_i)\cdot N_h(\tau_i). \quad (12)$$

The observed instantaneous third-order rate constants $k_2(\tau_i)$ and those calculated by equations (10), (11), and (12) are in Table 2 in columns 8, 9, 10, and 11, respectively.

It has been noted that the rate constants calculated by the over-all kinetic third-order equation depend on the initial mole proportion of the reacting compounds, therefore the reaction order equal to 2 on methanol cannot be considered as an established fact. For comparison with $k_2(\tau_i)$ the over-all instantaneous second- ($k_{2\text{-}\underline{II}}(\tau_i)$) and fourth- ($k_{2\text{-}\underline{IV}}(\tau_i)$) order rate constants (first and third order on methanol) were calculated by equation (5) and the following equation

$$w_2(\tau_i) = -k_{2\text{-}\underline{IV}}(\tau_i)\cdot C_2(\tau_i)\cdot[C_{alc.}(\tau_i)]^3.$$

The observed instantaneous second- and fourth-order rate constants and those calculated by equations (10), (11), and (12) are listed in Table 2 in columns 4, 5, 6, 7 and 12, 13, 14, 15, respectively. On this basis the reaction order on methanol should not be considered as a reliable fact, also

Table 2

No. of expt.	τ_i [hr]	$c_2(\tau_i)$ [mol./l.]	$k_{2-II}(\tau_i)\cdot 10^3$ [l./mol.·hr] observed	calc. by Eq. (10)	(11)	(12)	$k_2(\tau_i)\cdot 10^4$ [l^2/mol^2·hr] observed	calc. by Eq. (10)	(11)	(12)	$k_{2-IV}(\tau_i)\cdot 10^5$ [l^3/mol^3·hr] observed	calc. by Eq. (10)	(11)	(12)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	2	5.95	4.51	3.24	4.60	5.26					16.6	11.9	17.0	21.9
	3	5.82	4.38	3.28	4.24	4.58					17.8	13.1	17.4	19.9
	4	5.70	4.03	3.32	3.85	4.00					18.2	14.4	17.5	18.2
	5	5.59	3.49	3.35	3.50	3.58					17.2	15.6	17.4	16.9
	6	5.52	3.35	3.38	3.25	3.30					17.6	16.5	17.2	16.0
	7	5.44	2.93	3.40	2.99	3.04					16.5	17.5	16.8	15.2
	8	5.38	2.63	3.43	2.78	2.85					15.8	18.4	16.4	14.6
	9	5.32	2.44	3.45	2.58	2.67					15.5	19.3	16.0	14.0
2	2	4.18	5.85	4.57	6.06	5.67	6.13	4.77	6.26	7.14	6.42	5.14	6.69	6.72
	3	3.96	5.70	4.68	5.70	5.19	6.27	5.13	6.43	6.61	6.88	5.79	7.05	6.59
	4	3.77	5.56	4.77	5.29	4.84	6.38	5.47	6.40	6.24	7.31	6.43	7.19	6.55
	5	3.60	5.28	4.86	4.84	4.58	6.30	5.79	6.21	5.96	7.52	7.06	7.15	6.57
3	2	3.10	6.41	5.38	6.85	6.30	5.06	4.26	5.32	5.53	4.00	3.35	4.24	4.08
	3	2.85	6.54	5.51	6.70	6.06	5.39	4.55	5.54	5.38	4.44	3.73	4.56	4.21
	4	2.63	6.67	5.63	6.42	5.90	5.70	4.85	5.59	5.29	4.87	4.13	4.74	4.37
	5	2.44	6.69	5.74	6.07	5.80	5.91	5.12	5.50	5.29	5.23	4.51	4.81	4.57
	6	2.27	6.05	5.85	5.69	5.75	5.51	5.39	5.32	5.27	5.03	4.90	4.77	4.80
	7	2.13	5.94	5.94	5.34	5.74	5.55	5.62	5.10	5.30	5.19	5.23	4.69	5.02
	8	2.01	5.14	6.02	4.99	5.75	4.92	5.84	4.85	5.35	4.71	5.57	4.56	5.26
	9	1.92	4.28	6.08	4.73	5.77	4.17	6.01	4.64	5.41	4.06	5.83	4.44	5.46

Table 2 (continued)

1	2	3	4	5	6	7.	8	9	10	11	12	13	14	15
4	2	2.36	6.76	5.86	7.16	6.65	4.51	3.90	4.65	4.71	3.00	2.53	3.10	2.96
	3	2.12	7.41	6.00	7.19	6.56	5.09	4.13	4.90	4.68	3.50	2.77	3.37	3.10
	4	1.90	7.34	6.13	7.10	6.53	5.21	4.38	5.03	4.70	3.69	3.03	3.57	3.28
	5	1.72	7.04	6.24	6.93	6.55	5.12	4.59	5.05	4.75	3.72	3.26	3.68	3.47
	6	1.57	6.56	6.33	6.73	6.59	4.88	4.77	5.00	4.82	3.63	3.67	3.73	3.64
	7	1.46	6.05	6.40	6.55	6.64	4.57	4.91	4.93	4.88	3.46	3.63	3.74	3.80
	8	1.34	6.28	6.48	6.33	6.71	4.84	5.07	4.81	4.96	3.72	3.82	3.73	3.99
	9	1.24	6.29	6.55	6.11	6.79	4.91	5.21	4.69	5.05	3.84	3.99	3.70	4.17
5	2	2.20	7.08	5.96	7.20	6.70	4.57	3.85	4.55	4.56	2.95	2.42	2.94	2.80
	3	1.96	7.29	6.10	7.26	6.64	4.86	4.08	4.80	4.56	3.24	2.65	3.20	2.94
	4	1.77	7.05	6.21	7.21	6.64	4.82	4.28	4.91	4.59	3.30	2.85	3.36	3.09
	5	1.59	6.76	6.41	7.16	6.75	4.74	4.57	5.06	4.72	3.32	3.14	3.59	3.36
	6	1.46	6.40	6.40	6.95	6.71	4.56	4.62	4.93	4.70	3.25	3.21	3.54	3.41
	7	1.34	6.58	6.48	6.77	6.78	4.78	4.77	4.88	4.77	3.47	3.38	3.57	3.57
	8	1.23	6.40	6.55	6.58	6.85	4.72	4.92	4.80	4.85	3.49	3.54	3.58	3.74
	9	1.12	6.53	6.63	6.37	6.94	4.90	5.06	4.68	4.95	3.67	3.70	3.56	3.92
6	2	2.02	7.24	6.06	7.22	6.75	4.51	3.77	4.40	4.39	2.81	2.27	2.74	2.60
	3	1.79	7.56	6.19	7.30	6.72	4.85	3.98	4.63	4.40	3.10	2.47	2.97	2.74
	4	1.60	7.80	6.30	7.29	6.73	5.13	4.17	4.75	4.44	3.37	2.66	3.14	2.89
	5	1.42	7.77	6.41	7.20	6.78	5.23	4.36	4.82	4.51	3.52	2.85	3.26	3.05
	6	1.26	7.60	6.51	7.06	6.86	5.22	4.53	4.81	4.59	3.59	3.02	3.33	3.22
	7	1.14	7.40	6.59	6.90	6.94	5.17	4.68	4.76	4.67	3.62	3.17	3.37	3.39
7	2	2.02	6.96	6.06	7.19	6.77	4.28	3.72	4.32	4.36	2.63	2.21	2.65	2.54
	3	1.79	7.48	6.19	7.31	6.73	4.73	3.93	4.57	4.36	3.00	2.41	2.90	2.68
	4	1.59	7.19	6.31	7.32	6.75	4.67	4.13	4.72	4.41	3.03	2.59	3.07	2.82
	5	1.44	6.42	6.40	7.26	6.79	4.25	4.28	4.78	4.56	2.82	2.75	3.18	2.96
	6	1.33	6.71	6.47	7.18	6.83	4.51	4.40	4.80	4.51	3.03	2.87	3.25	3.07
	7	1.20	7.10	6.55	7.06	6.91	4.86	4.55	4.78	4.58	3.33	3.01	3.31	3.22

Table 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
8	1	0.935	6.30	6.67	6.83	6.96	2.96	3.15	3.17	3.32	1.39	1.40	1.48	1.48
	1.5	0.871	6.89	6.70	6.94	6.98	3.26	3.19	3.24	3.33	1.54	1.43	1.53	1.50
	2	0.808	7.21	6.74	7.04	6.70	3.43	3.23	3.32	3.34	1.63	1.45	1.58	1.52
	2.5	0.748	7.70	6.77	7.12	7.02	3.69	3.26	3.39	3.35	1.77	1.48	1.62	1.55
	3	0.686	7.80	6.80	7.21	7.04	3.76	3.30	3.46	3.37	1.81	1.51	1.66	1.57
	3.5	0.634	7.67	6.83	7.28	7.06	3.71	3.34	3.51	3.38	1.80	1.53	1.70	1.59
	4	0.586	7.48	6.86	7.35	7.09	3.64	3.37	3.56	3.40	1.77	1.55	1.74	1.61
	4.5	0.547	7.34	6.89	7.39	7.11	3.58	3.39	3.60	3.41	1.75	1.57	1.76	1.63
	5	0.505	7.59	6.91	7.44	7.13	3.72	3.42	3.64	3.43	1.82	1.59	1.79	1.65
9	2	0.163	6.73	7.04	6.67	6.95	2.82	2.98	2.81	2.88	1.18	1.18	1.17	1.16
	3	0.139	6.65	7.06	6.71	6.96	2.79	3.00	2.84	2.88	1.17	1.18	1.19	1.16
	4	0.119	6.77	7.07	6.75	6.97	2.85	3.01	2.86	2.89	1.20	1.19	1.20	1.17
	5	0.101	6.97	7.08	6.79	6.98	2.93	3.02	2.88	2.89	1.23	1.20	1.21	1.17
	6	0.086	6.79	7.08	6.80	6.98	2.85	3.03	2.90	2.90	1.20	1.20	1.22	1.18
	7	0.073	6.75	7.09	6.83	6.99	2.84	3.03	2.91	2.90	1.20	1.20	1.23	1.18
10	2	0.047	7.38	7.09	6.59	6.92	3.02	2.94	2.73	2.80	1.24	1.13	1.11	1.10
	3	0.039	6.70	7.10	6.60	6.93	2.74	2.95	2.73	2.80	1.12	1.14	1.12	1.10
	4	0.034	6.35	7.10	6.61	6.93	2.60	2.95	2.74	2.80	1.36	1.14	1.12	1.10
	5	0.030	5.86	7.10	6.62	6.93	2.40	2.95	2.74	2.80	0.98	1.14	1.12	1.10
	6	0.026	6.52	7.10	6.63	6.94	2.67	2.95	2.75	2.81	1.10	1.14	1.12	1.11
	7	0.021	6.83	7.11	6.63	6.94	2.80	2.96	2.75	2.81	1.15	1.14	1.13	1.11
	8	0.018	6.65	7.11	6.64	6.94	2.73	2.96	2.76	2.81	1.12	1.14	1.13	1.11
11	2	1.93	5.82	5.26	5.64	5.65	3.61	3.35	3.59	3.73	2.25	2.04	2.14	2.23
	3	1.75	5.80	5.74	5.74	5.67	3.68	3.49	3.73	3.77	2.34	2.17	2.30	2.34
	4	1.58	5.94	5.41	5.80	5.72	3.85	3.62	3.83	3.83	2.50	2.30	2.43	2.47
	5	1.46	5.42	5.47	5.82	5.77	3.58	3.73	3.88	3.86	2.36	2.41	2.53	2.58
	6	1.36	5.12	5.52	5.81	5.82	3.42	3.81	3.90	3.94	2.28	2.50	2.59	2.67
	7	1.25	5.55	5.57	5.78	5.89	3.76	3.91	3.90	4.00	2.55	2.60	2.66	2.79

Table 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
12	2	2.97	2.76	2.89	2.31	2.15	2.45	2.74	2.30	2.14	2.17	2.48	1.81	1.72
	3	2.87	2.98	2.90	2.33	2.15	2.69	2.81	2.31	2.16	2.43	2.58	1.90	1.77
	4	2.78	2.90	2.92	2.33	2.15	2.67	2.87	2.31	2.18	2.45	2.69	1.98	1.84
	5	2.70	2.77	2.93	2.35	2.16	2.59	2.93	2.30	2.20	2.42	2.78	2.05	1.90
	6	2.62	2.51	2.95	2.34	2.17	2.38	2.99	2.28	2.22	2.26	2.87	2.10	1.95
	7	2.56	2.32	2.96	2.34	2.18	2.22	3.03	2.26	2.24	2.13	2.94	2.15	2.01
	8	2.50	2.36	2.97	2.33	2.19	2.29	3.08	2.24	2.26	2.22	3.01	2.19	2.06
	9	2.44	2.45	2.98	2.32	2.20	2.41	3.12	2.22	2.29	2.36	3.09	2.22	2.12
13	2	2.66	2.60	3.10	2.60	2.56	2.12	2.72	2.40	2.34	1.74	2.25	1.72	1.77
	3	2.57	2.63	3.11	2.63	2.57	2.18	2.77	2.41	2.36	1.81	2.32	1.80	1.83
	4	2.49	2.71	3.12	2.65	2.58	2.28	2.82	2.42	2.39	1.91	2.40	1.86	1.88
	5	2.41	2.61	3.15	2.66	2.60	2.22	2.87	2.42	2.41	1.89	2.47	1.92	1.94
	6	2.34	2.61	3.16	2.67	2.62	2.25	2.92	2.42	2.44	1.94	2.54	1.98	2.01
	7	2.27	2.56	3.17	2.67	2.63	2.23	2.97	2.41	2.47	1.94	2.61	2.03	2.07
	8	2.21	2.39	3.19	2.67	2.65	2.11	3.02	2.39	2.50	1.86	2.68	2.07	2.13
	9	2.15	2.37	3.20	2.66	2.67	2.11	3.06	2.37	2.53	1.88	2.74	2.11	2.19
14	2	1.88	4.32	3.77	3.46	3.76	2.95	2.76	2.66	2.81	2.02	1.88	1.60	1.87
	3	1.76	4.21	3.80	3.52	3.81	2.93	2.83	2.70	2.86	2.03	1.96	1.69	1.97
	4	1.66	3.87	3.83	3.56	3.86	2.72	2.89	2.72	2.92	1.92	2.03	1.77	2.05
	5	1.58	3.31	3.85	3.59	3.91	2.36	2.94	2.73	2.97	1.68	2.09	1.83	2.13
	6	1.52	3.57	3.86	3.61	3.94	2.57	2.98	2.73	3.00	1.84	2.13	1.86	2.19
	7	1.44	3.97	3.88	3.62	3.99	2.88	3.03	2.73	3.06	2.09	2.19	1.92	2.27
15	2	1.64	2.47	2.41	2.03	2.29	1.98	2.10	1.96	2.00	1.58	1.66	1.29	1.56
	3	1.59	2.40	2.41	2.06	2.32	1.94	2.13	1.96	2.03	1.56	1.69	1.33	1.61
	4	1.55	2.35	2.42	2.08	2.35	1.91	2.14	1.96	2.07	1.55	1.72	1.36	1.65
	5	1.51	2.53	2.42	2.09	2.37	2.07	2.16	1.96	2.10	1.69	1.74	1.39	1.70
	6	1.46	2.79	2.43	2.11	2.41	2.30	2.18	1.95	2.14	1.90	1.77	1.42	1.75
	7	1.40	2.51	2.43	2.14	2.45	2.09	2.21	1.94	2.19	1.74	1.81	1.47	1.83

Table 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
16	2	1.158	1.00	1.06	1.20	1.14	1.21	1.33	1.50	1.39	1.46	1.43	1.76	1.57
	3	1.147	1.08	1.06	1.20	1.15	1.30	1.34	1.49	1.40	1.57	1.44	1.77	1.59
	4	1.136	1.08	1.06	1.21	1.15	1.31	1.34	1.49	1.41	1.59	1.44	1.78	1.61
	5	1.126	1.14	1.06	1.21	1.16	1.38	1.34	1.48	1.43	1.68	1.45	1.80	1.63
	6	1.116	1.21	1.06	1.22	1.17	1.47	1.34	1.49	1.44	1.79	1.46	1.81	1.65
	7	1.104	1.18	1.06	1.22	1.18	1.44	1.35	1.47	1.45	1.76	1.46	1.83	1.67
17	2	1.014	1.13	1.00	1.23	1.19	1.40	1.28	1.53	1.49	1.73	1.39	1.88	1.72
	3	1.004	1.25	1.00	1.23	1.20	1.55	1.28	1.52	1.49	1.92	1.39	1.90	1.74
	4	0.994	1.36	1.00	1.24	1.20	1.70	1.28	1.52	1.50	2.11	1.40	1.91	1.76
	5	0.983	1.39	1.00	1.24	1.21	1.73	1.29	1.51	1.52	2.16	1.40	1.93	1.79
	6	0.970	1.41	1.00	1.25	1.22	1.77	1.29	1.51	1.53	2.21	1.41	1.93	1.81
	7	0.960	1.37	1.00	1.25	1.23	1.72	1.29	1.50	1.55	2.15	1.41	1.96	1.84

The rate constants calculated by equation (12) (in the corresponding solvents) are as follows:

$K_{2-\bar{II}} = 1.317 \cdot 10^{-5}$
$K_{alc.-\bar{II}} = 1.062 \cdot 10^{-5}$
$K_{3-\bar{II}} = 9.108 \cdot 10^{-2}$
$K_{h-\bar{II}} = 1.222 \cdot 10^{-7}$
$K_{2-h-\bar{II}} = 5.533 \cdot 10^{-30}$

$K_2 = 3.64 \cdot 10^{-5}$
$K_{alc.} = 6.417 \cdot 10^{-9}$
$K_3 = 3.171 \cdot 10^{-3}$
$K_h = 8.260 \cdot 10^{-9}$
$K_{2-h} = 4.995 \cdot 10^{-33}$

$K_{2-\bar{IV}} = 6.311 \cdot 10^{-6}$
$K_{alc.-\bar{IV}} = 5.633 \cdot 10^{-12}$
$K_{3-\bar{IV}} = 2.904 \cdot 10^{-2}$
$K_{h-\bar{IV}} = 7.006 \cdot 10^{-10}$
$K_{2-h-\bar{IV}} = 2.310 \cdot 10^{-37}$

In Table 2 the experimental numbers and the mole proportions $n_2(\tau_0):n_{alc.}(\tau_0):n_{HCl}(\tau_0)$ are as follows:

1 - 1 : 0.93 : 0
2 - 1 : 2.25 : 0
3 - 1 : 3.77 : 0
4 - 1 : 5.60 : 0
5 - 1 : 6.10 : 0
6 - 1 : 6.75 : 0
7 - 1 : 6.91 : 0
8 - 1 : 20.3 : 0
9 - 1 : 107 : 0
10 - 1 : 362 : 0
11 - 1 : 7.32 : 0.34
12 - 1 : 3.69 : 0.94
13 - 1 : 4.45 : 1.02
14 - 1 : 7.11 : 1.17
15 - 1 : 7.26 : 2.72
16 - 1 : 7.09 : 7.28
17 - 1 : 7.88 : 8.60

the best results (i.e. the minimum value of the deviation squares sum) have been obtained for the second order on methanol.

Taking into account the literature data about the fact that methanol is associated[18] and the solutions of hydrogen chloride in methanol consist of complexes (ion-pairs[9]) practically, dimethylchlorothiophosphate may be assumed as reacting with monomers and associated molecules of methanol and also with complexes of hydrogen chloride with methanol. The complexes of dimethylchlorothiophosphate with methanol may be well decomposed in the first-order reaction.

If one introduses the non-linear terms into models (11) and (12), it is necessary to specify the physical meaning of the non-linear term constants (there are literature data about using non-linear models to describe a variety of processes, for example the correlation between the reactivity of substituted phosphinic acids and their structure[19]). One can interprete the constants in equations (11) and (12) as a ratio of rate constants of some solvation processes. In such a case the presence of a non-linear term in equations (11) and (12) can be explained by breaking these solvation processes with changes in a type of a solvent (for example, with transition from dimethylchlorothiophosphate to methanol). Let us assume that the Palm[16,17] rate constants of a solvation process can be described by the following equation

$$\ln K_1 = N_1 \cdot \ln K_1^1 + N_2 \cdot \ln K_1^2 ,$$

and another solvation process - by the equation

$$\ln K_2 = N_1 \cdot \ln K_2^1 + N_2 \cdot \ln K_2^2 .$$

Then as a result of simple algebraic transformation one will obtain the following equation for the over-all rate constants K ($\ln K = N_1 \cdot \ln k_1 + N_2 \cdot \ln K_2$):

$$\ln K = N_1 \cdot \ln K_1^1 + N_2 \cdot \ln K_2^2 + N_1 \cdot N_2 \cdot \ln(K_1^2 \cdot K_2^1 / K_1^1 \cdot K_2^2).$$

In such a case it is possible to apply the thermodynamic ratios to the rate constants of equation (12) (and to the non-linear rate constant $K_{2\text{-}h}(\tau_i)$).

Table 3

No. of Expt.	τ_i [hr]	$k_2(\tau_i)\cdot10^4$ observed	$k_2(\tau_i)\cdot10^4$ calc. by Eq. (13)
1	2	3	4
		T = 298°K	
1	2	8.64	10.7
	3	8.83	9.75
	4	8.56	8.89
	5	7.75	8.23
	6	7.68	7.79
	7	6.96	7.38
	8	6.44	7.05
	9	6.16	6.75
2	2	6.13	6.22
	3	6.27	5.91
	4	6.38	5.68
	5	6.30	5.52
3	2	5.06	5.08
	3	5.39	5.01
	4	5.70	4.98
	5	5.91	4.98
	6	5.51	5.02
	7	5.55	5.06
	8	4.92	5.13
	9	4.17	5.18
4	2	4.51	4.46
	3	5.09	4.47
	4	5.21	4.51
	5	5.12	4.57
	6	4.88	4.64
	7	4.57	4.70
	8	4.84	4.78
	9	4.91	4.86
5	2	4.57	4.70
	3	4.86	4.37
	4	4.82	4.42
	5	4.74	4.56
	6	4.56	4.54
	7	4.78	4.61
	8	4.72	4.69
	9	4.90	4.78
6	2	4.51	4.21
	3	4.85	4.25
	4	5.13	4.30
	5	5.23	4.37
	6	5.22	4.45
	7	5.17	4.53
7	2	4.28	4.19
	3	4.73	4.22
	4	4.67	4.27
	5	4.25	4.33
	6	4.51	4.38
	7	4.86	4.45
8	1	2.96	3.35
	1.5	3.26	3.36
	2	3.43	3.37
	2.5	3.69	3.39
	3	3.76	3.40
	3.5	3.71	3.42
	4	3.64	3.44
	4.5	3.58	3.45
	5	3.72	3.46
9	2	2.82	2.99
	3	2.79	2.99
	4	2.85	3.00
	5	2.93	3.00
	6	2.85	3.01
	7	2.84	3.01
10	2	3.02	2.92
	3	2.74	2.92
	4	2.60	2.92
	5	2.40	2.93
	6	2.67	2.93
	7	2.80	2.93
	8	2.73	2.93
11	2	3.62	3.64
	3	3.68	3.69
	4	3.85	3.74
	5	3.58	3.80
	6	3.42	3.85
	7	3.76	3.91
12	2	2.45	2.24
	3	2.69	2.25
	4	2.67	2.74
	5	2.59	2.30
	6	2.38	2.32
	7	2.22	2.34
	8	2.29	2.36
	9	2.41	2.38
13	2	2.12	2.40
	3	2.18	2.42
	4	2.28	2.45
	5	2.22	2.47
	6	2.25	2.50
	7	2.23	2.53
	8	2.11	2.55
	9	2.11	2.58
14	2	2.95	2.80
	3	2.93	2.85
	4	2.72	2.90
	5	2.36	2.95
	6	2.57	2.98
	7	2.88	2.93
15	2	1.98	2.03
	3	1.94	2.07
	4	1.91	2.09
	5	2.07	2.12
	6	2.30	2.15
	7	2.09	2.19

Table 3 (continued)

1	2	3	4	1	2	3	4	1	2	3	4
16	2	1.21	1.39	19	2	14.0	14.0	22	2	57.9	46.0
	3	1.30	1.40		3	12.8	13.3		3	49 5	45.3
	4	1.31	1.41		4	12.3	13.4		4	44.9	45.2
	5	1.38	1.41		5	11.8	13.5		5	45.6	45.2
	6	1.47	1.43		6	11.6	13.7		6	47.5	45.4
	7	1.44	1.44		7	11.2	14.0		7	57.9	45.6
					8	10.4	14.2		8	62.4	46.0
17	2	1.40	1.45		9	11.5	15.4		9	66.0	46.4
	3	1.55	1.46								
	4	1.70	1.47					23	1	42.1	51.8
	5	1.73	1.48			T = 323°K			1.5	47.8	44.6
	6	1.77	1.49						2	44.6	52.6
	7	1.72	1.50	20	2	50.3	44.9		2.5	42.0	53.0
					3	43.9	43.6		3	42.0	53.3
					4	43.0	42.8		3.5	42.2	53.6
		T = 308°K			5	41.7	42.4		4	42.6	53.8
					6	40.6	42.1		4.5	45.7	54.0
					7	42.0	42.0		5	48.9	54.2
18	2	20.9	17.4		8	45.2	41.9		5.5	48.9	54.3
	3	16.8	16.1		9	43.7	41.9				
	4	16.8	15.0					24	3	25.2	32.7
	5	16.5	14.0						4	27.8	32.4
	6	15.0	13.2	21	2	36.9	29.5		5	31.6	32.1
	7	13.4	12.8		3	43.5	28.8		6	38.7	31.9

In Table 3 the experimental numbers and the mole proportions $n_2(\tau_0):n_{alc.}(\tau_0):n_{HCl}(\tau_0)$ are as follows:

1 - 1:0.93:0	9 - 1:107:0	17 - 1:7.88:8.60
2 - 1:2.25:0	10 - 1:362:0	18 - 1:0.93:0
3 - 1:3.77:0	11 - 1:7.32:0.34	19 - 1:3.10:0
4 - 1:5.60:0	12 - 1:3.69:0.94	20 - 1:0.83:0
5 - 1:6.10:0	13 - 1:4.45:1.02	21 - 1:1.07:0.62
6 - 1:6.75:0	14 - 1:7.11:1.17	22 - 1:3.10:0
7 - 1:6.91:0	15 - 1:7.26:2.72	23 - 1:5.96:0
8 - 1:20.3:0	16 - 1:7.09:7.28	24 - 1:1.39:0.62

T_{ik} = 325°K
ΔS_2 = -6.865 cal/mol.
$\Delta S_{alc.}$ = 57.695 -"-
ΔS_3 = -59.092 -"-
ΔS_h = 64.915 -"-
ΔS_{2-h} = 429.4 -"-
ΔH° = 3258.2 cal/mol.

According to the well-known LFFR [17] rule there is the linear correlation between ΔH and ΔS, if a substituent, a reagent or a solvent is changed. We have applied equation (13) to find the isokinetic temperature T_{ik}:

$$R \cdot \ln k_2(\tau_i) = (1 - T_{ik}/T) \cdot [\sum_j N_j(\tau_i) \cdot \Delta S_j + N_{2-h}(\tau_i) \cdot \Delta S_{2-h}] - \Delta H^\circ/T \cdot [1 + N_2(\tau_i) \cdot N_h(\tau_i)] \quad , \qquad (13)$$

where ΔS_j is a change in the entropy of the reaction of dimethylchlorothiophosphate with methanol in "j-solvent", ΔH° is a change in the enthalpy of the reaction of dimethylchlorothiophosphate with methanol.

For the five-parameter model (12) the satisfactory correlation has been found between the observed third-order rate constants and those calculated by equation (13) at temperatures 25°, 35° and 50°C (see Table 3).

The logarithms of the rate constants K_2, $K_{alc.}$, K_3, K_h, and K_{2-h} at temperatures 25°, 35° and 50°C are given in Table 4.

Table 4

The Logarithms of the Rate Constants	25°C	35°C	50°C
$\ln K_2$	-5.1876	-5.1315	-5.0536
$\ln K_{alc.}$	-8.1479	-6.9406	-5.2699
$\ln K_3$	-2.7930	-3.6679	-4.8784
$\ln K_h$	-8.4789	-7.1430	-5.2940
$\ln K_{2-h}$	-25.1913	-17.3571	-6.5150

The isokinetic dependence (according to equation (13)) means that the observed rate constants can be described by the five-parameter equation (12) not only for temperatures 35° and 50°C, but for any temperature in the interval under study (to find the model for temperatures 35° and 50°C the same volume of experimental data as for 25°C is necessary).

References

1. J.C.Jungers and L.Sajus. L ànalyse cinétique de la transformation chimiqe. Paris, 1967.
2. N.M.Loznikova, Yu.N.Sapozhkov, and K.D.Shvetsova-Shilovskaya, Zh.org.khim., 46, 1761, 1976.
3. A.Weissberger and E.S.Proskauer,Organic Solvents.Physical Properties and Methods of Purification, N.-Y., L., 1955.
4. V.I.Vigdorovich and I.I.Gorelkin, Zh.prikl.khim., 46, 1083, 1973.
5. A.Savitzky and M.Golay, Anal.Chem., 36, 1627, 1964.
6. A.O.Kôrgesaar,V.G.Timotheus, and V.A.Palm, Correlation Equations in Organic Chemistry,Tartu,1,265,1962(in Russ.)
7. H.A.Smith, J.Am.Chem.Soc., 62, 1136,1940.
8. V.Palm, A.Adermann, and A.Kôrgesaar, Acta et comment univ.Tartuensis, 95, 24, 1960.
9. V.A.Palm and A.O.Kôrgesaar, Reakts.sposobn.organ.soedin., 1, 157, 1964.
10. N.I.Vrzhosek,N.G.Doropheeva, and O.K.Kudra, Ukr.khim.zh., 37, 328, 1971.
11. V.I.Vigdorovich and V.A.Zhukov,Zh.phys.khim.,48,578,1974.
12. V.I.Vigdorovich and V.A.Zhukov,Reph.zh.khim.,18 999,1974.
13. A.O.Kôrgesaar and V.A.Palm, Reakts. sposobn.organ.soedin., 11, 145, 1974.
14. V.A.Palm and A.O.Kôrgesaar, Organic Reactivity, 11, 519, 1974.
15. A.O.Kôrgesaar and V.A.Palm, Organic Reactivity, 11, 693, 1975.
16. V.A.Palm, Reakts. sposobn. organ. soedin., 1, 128, 1964.
17. V.A.Palm,Fundamentals of Quantitative Theory of Organic Reactions, "Khimiya", L., 1977.
18. V.A.Grigoryeva, V.V.Komratova, L.S.Bekhly, S.M.Baturin, R.P.Tiger, and S.G.Entelis, Kinetika i kataliz, 13, 653, 1972.
19. I.A.Koppel and V.A.Palm, Reakts. sposobn. organ. soedin., 4, 381, 1967.

Substituted Hydrazides of Hydroxylcarboxylic Acids. C VII. The Kinetics of Acetylation of Arylhydrazides of Dibutylglycolic Acid with Acetic Anhydride.

I.Berdinskii, G.Posyagin, and G.Belousov

Perm Sate University, Perm

Received May 18, 1979

The kinetics of acetylation of arylhydrazides of dibutylglycolic acid with acetic anhydride in benzene at 25,40,55 and 70°C has been studied. A correlation between the lgK values and the corresponding Hammett σ constants characteristic of the polar effect of the substituted phenyls, has been found. The reaction mechanism has been suggested.

The kinetics of acylation of arylhydrazides of disubstituted glycolic acids with acid chlorides of different carboxylic acids was investigated elsewhere [1-9]. It is interesting to study the kinetics of acylation of these compounds with other acylating agents, for example with anhydrides of carboxylic acids.

It is known that with acylation of arylamines and benzhydrazides, whose chemical structure is similar to arylhydrazides, with anhydrides of carboxylic acids the strong autocatalysis takes place due to the acid formed during the reaction course [10-14].

This report is devoted to the problem whether this effect works with substituted hydrazides of hydroxylcarboxylic acids. We have studied the kinetics of acetylation of arylhydrazides of dibutylglycolic acid [15-18] with acetic anhydride in benzene at 25,40,55 and 70°C. The reaction scheme can be shown as follows:

$$XC_6H_4NHNHCOC(OH)(C_4H_9)_2 + (CH_3CO)_2O \xrightarrow{-CH_3COOH} XC_6H_4N(COCH_3)NHCOC(OH)(C_4H_9)_2$$

X=H, p- , m-CH_3, p- , m-CH_3O, p- , m - Cl.

The method of kinetic measurements with the use of quantitative determination of unreacted arylhydrazide by means of polarography has been described elsewhere [2].

The typical kinetic data are tabulated (Tables 1 and 2). Table 3 shows general kinetic information where "a" and "b" denote the initial concentration of acetic anhydride and arylhydrazide; $\bar{K}$, E_a, A, and $\Delta S^{\#}$ denote the values of the average rate constants, activation energies, and preexponential in the Arrhenius equation and activation entropy, respectively.

Table 1. Kinetics of Acetylation of p-Chlorphenylhydrazide of Dibutylglycolic Acid at 40°C.

Time (min.)	0	60	120	180	240	300
i_l μA	2.77	2.47	2.17	1.95	1.73	1.50
$K \cdot 10^4$ l/mole·sec	-	0.98	1.04	1.00	1.01	1.05
$\bar{K} \cdot 10^4$ l/mole·sec	1.02 ± 0.02					

Table 2. Kinetics of Acetylation of p-Anisilhydrazide of Dibutylglycolic Acid at 55°C.

Time (min.)	0	4	8	12	16	20
i_l μA	2.50	2.11	1.73	1.45	1.15	1.00
$K \cdot 10^4$ l/mole·sec	-	82.9	89.7	88.5	94.7	89.2
$\bar{K} \cdot 10^4$ l/mole·sec	89.0 ± 2.6					

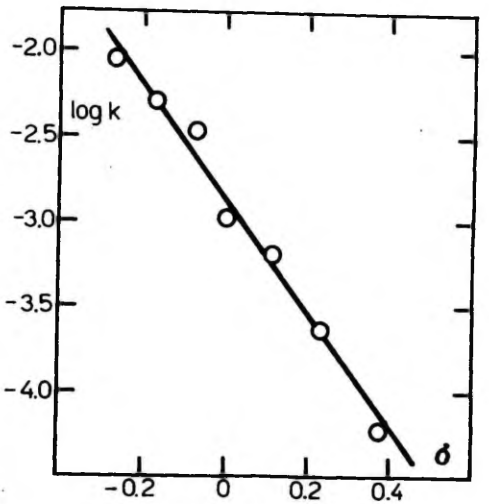
Table 3- Kinetics of Acetylation of Arylhydrazides of Dibutylglycolic Acid $XC_6H_4NHNHCOC(OH)(C_4H_9)_2$ with Acetic Anhydride. General Kinetic Information

X	a·10⁴ mol/l	b·10⁴ mole/l	$\bar{K}\cdot 10^4$ l/mole·sec 25°C	40°C	55°C	70° C	E_A KJ/mole	A l/mole·sec	$\Delta S^{\neq}$ cal/mole·grade
p-CH_3O	909	18.18	-	30.0±1.1	89.0±2.6	186±14	54.4	$3.78\ 10^6$	-30.5
p-CH_3	909	18.18	-	12.1±1.2	52.4±1.5	168± 6	78.2	$1.47\ 10^{10}$	-14.2
m-CH_3	3333	16.7}25°	3.39±	9.46±0.51	35.3±1.7	85.7±8.5	62.2	$2.69\ 10^7$	-26.9
	909	18.18	±0.15						
H	3333	16.7}25°	1.37±	4.19±0.25	10.6±1.7	29.1±3.7	57.1	$1.41\ 10^6$	-32.4
	909	18.18	±0.10						
m-CH_3O	1818	9.09	-	3.58±0.13	7.18±0.32	28.2±1.5	61.0	$4.87\ 10^6$	-29.7
p-CL	3333	16.7	-	1.02±0.02	2.34±0.28	6.55±0.34	55.1	$1.56\ 10^5$	-36.7
m-CL	4615	15.4	-	0.210±0.014	0.532±0.026	1.88±0.17	64.9	$1.37\ 10^6$	-32.4

One can see from Table 3 that the nature and the position of the substituent in the benzene ring at the nitrogen atom influence markedly the rate of acetylation of these compounds.

To estimate the influence the Hammett equation was used. In Figure 1 the values of lgK are plotted vs.Hammett σ-constants.

Figure 1. Plot of lgK vs.Hammet σ-constants at 55° C.



The correlation parameters between the lgK and σ-constants are given in Table 4.

Table 4.The Correlation Parameters.

t^{o} c	r	s	ρ	Sp	$(lgK_o)_{calcd}$
40	o.981	0.155	-3.149	0.281	-3.329
55	0.989	0.129	-3.481	0.234	-2.868
70	0.978	0.167	-3.219	0.304	-2.414

For this reaction series the ρ-constant is almost equal to the analogous constant of the reaction of acylation of arylhydrozides of dibutylglycolic acid with benzoylchloride [1].

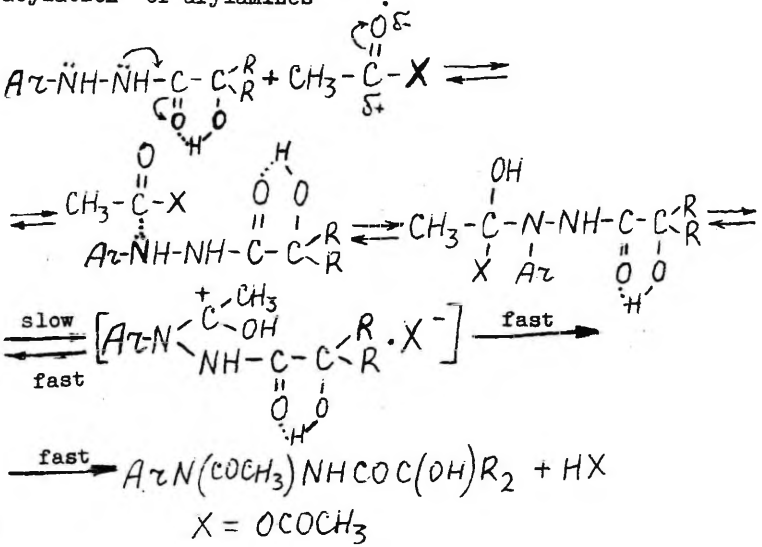
The data given in Tables 1 and 2 show that the rate constants calculated by means of the equation of pseudomonomolecular reaction [2] have small deviations from their average values and don't increase monotonously with the reaction time. This indicates that no autocatalysis takes place with acetylation of arylhydrazides of dibutylglycolic acid with acetic anhydride.To confirm this additional kinetic measurements were carried out with the addition of acetic acid to the reaction mixture. No changes in the reaction rate were observed.

This difference between the chemical properties of arylhydrazides of disubstituted glycolic acids and arylamines (or benzhydrazides) can be explained as follows: intermediate compounds I (see the scheme of the reaction mechanism) appearing as a result of interaction of arylhydrazides with acetic anhydride don't form cyclic transition complexes with the acid [11,12] because of the steric and polar effects of acyl of disubstituted glycolic

acid and the possible formathion of the intramolecular hydrogen bond between X and the hydrogen of amide nitrogen.

The kinetic data of this communication show that there is no appreciable difference in mechanism of non-catalytic acylation of arylhydrazides of dibutylglycolic acid with acetic anhydride and benzoylchloride. For example, the -constants for both series are almost equal. The values of activation energies and activation entropies don't differ appreciably for the two reaction series*.

Thus the reaction of acetylation of arylhydrazides of disubstituted qlycolic acids can be presented as follows in accordance with the mechanism suggested for non-catalytic acylation of arylamines[10,11]:



---

* The values of activation entrropies were not given in Ref. [1]. The calculations were done by us at present and $\Delta S^{\neq}$ = - 34 - - 40 $\frac{cal}{mol.grade}$

References

1. G.S.Posyagin, V.P.Ust-Katchkintsev, and I.S.Berdinskii, Utchon.Zapiski Perm Univers.(USSR),141,327(=1966).
2. I.S.Berdinskii, G.S.Posyagin, V.P.Ust-Katchkintsev, and N.P.Glukhev, Reakts.sposobn.organ.soed.(USSR),4 ,96(1967).
3. I.S.Berdinskii, G.S. Posyagin, and V.P.Ust-Katchkinsev, Reakts. sposobn. organ. soed.(USSR), 4,330(1967).
4. I.S.Berdinskii,G.P.Piskunova, G.S.Posyagin, E.S.Ponosova, and I.M.Shevaldina, Zh.organ.khim.(USSR),3, 1645 (1967).
5. I.S.Berdinskii, G.S.Posyagin, and V.P.Ust-Katchkinsev, Reakts. sposobn. organ. soed. (USSR).5, 350 (1968).
6. I.S.Berdinskii, G.S.Posyagin, and L.N.Starostina, Reakts. sposobn. organ. soed. (USSR), 6, 129 (=1969).
7. I.S.Berdinskii, L.N.Starostina, G.S.Posyagin and L.V.Gorshkova,Tr.Ural Univers.,Org.khim.(USSR),2,69(1973).
8. I.S.Berdinskii, G.S.Posyagin, and L.S.Nikulina, Reakts. sposobn.organ.soed. (USSR), 8, 637 (1971).
9. G.S.Posyagin,I.S.Berdinskii, and G.B.Petrova, Reakts. sposobn.organ.soed. (USSR), 11, 355 (1974).
10. L.M.Litvinenko and D.M.Aleksandrova,Ukr. khim.zh. (USSR), 27, 212 (1961).
11. N.M.Oleinik, M.N.Sorokin, and L.M.Litvinenko, Ukr.khim. zh. (USSR), 38, 343 (1972).
12. L.M.Litvinenko, N.M.Oleinik, and L.P.Kurtchenko, Reakts. sposobn.organ.soed.(USSR), 6, 832 (1969).
13. A.P.Grekov and V.K.Skriptchenko, Zh.organ.khim. (USSR), 3, 1251 (1967).
14. A.P.Grekov and V.K.Skriptchenko, Zh.organ.khim. (USSR), 3, 1287 (1967).
15. I.S.Berdinskii, Zh.obshch.khim. (USSR),28, 1263 (1958).
16. I.S.Berdinskii and I.D.Yatskova, Zh.obshch.khim. (USSR), 33, 943 (1963).
17. I.S.Berdinskii, N.N.Pugina, N.D.Bushina, and P.V.Kerepanova, Zh.organ.khim. (USSR), 1, 953 (1965).
18. I.S.Berdinskii, S.D.Alekseeva, A.P.Perevosohikova, and N.A.Kostareva, Zh.organ.khim. (USSR), 2, 318 (1966).

KINETIC STUDY OF HYDROLYSIS OF BENZOATES. XIII. ALKALINE HYDROLYSIS OF $N(CH_3)_3^+$ SUBSTITUTED ALKYL BENZOATES IN THE PRESENCE OF $NaClO_4$ AND NaCl .

V. Nummert and M. Piirsalu

Laboratory of Chemical Kinetics and Catalysis,
Tartu State University, Tartu, Est.SSR

Received June 10, 1979

The kinetics of alkaline hydrolysis of $N(CH_3)_3^+$ substituted alkyl benzoates $C_6H_5COO(CH_2)_nN(CH_3)_3^+$ (n= 1,2, and 3) is studied as a function of the concentration of $NaClO_4$ and NaCl at 50°C in water. For all alkyl benzoates studied negative salt effects were detected. With $NaClO_4$ the effects are much higher than those observed with NaCl.

Purely electrostatic components of the salt effects were calculated by subtracting specific components of the salt effect from the corresponding gross values for charged substituents. The purely electrostatic components are independent of the nature of a salt added.

The NaCl effect on the kinetics of the alkaline hydrolysis of some substituted phenyl tosylates and also phenyl and alkyl benzoates with charged and electroneutral substituents has been studied elsewhere [1-10]. Our previous works [11-14] list the data on the $NaClO_4$ effect on the kinetics of the alkaline hydrolysis of substituted phenyl benzoates with charged and electroneutral substituents, alkyl benzoates and phenyl tosylates with electroneutral substituents. The values of specific salt effects for electroneutral substituents have been found to depend linearly on the lgk_o values where

k_o is a rate constant at a zero concentration of electrolyte added.

On the basis of data on the salt effects for the alkaline hydrolysis of substituted phenyl benzoates, in the presence of $NaClO_4$ and NaCl an attempt has been made to estimate purely electrostatic components of the salt effects for charged substituents by subtracting the values of specific salt effect from the corresponding over-all effects.

These values obtained on the basis of the data about the $NaClO_4$ and NaCl effects, appeared to be essentially the same.

It is of interest to verify whether the electrostatic components are also constant for the charged substituents in the alkyl part of benzoates.

Experimental

The influence of $NaClO_4$ and NaCl on the kinetics of alkaline hydrolysis of alkyl benzoates with the general formula $C_6H_5COO(CH_2)_nN(CH_3)_3^+ X^-$ (where n = 1,2, and 3) has been studied at 50°C in water.

Formocholine - benzoate chloride was synthesized according to Ref. 15. The product was recrystallized from acetone. M.p. is 194°C. The NaCl effect on the kinetics of alkaline hydrolysis of formocholine - benzoate chloride up to ionic strength 0.4 was studied elsewhere.[4].

Choline - benzoate - iodide. The product of "Chemapol" was used without additional purification. The dependence of the alkaline hydrolysis kinetics on NaCl was studied over a broad range of ionic strenght elsewhere[4].

3 - trimethylammoniumpropyl benzoate iodide was synthesized in M. Lomonosov Institute of Chemical Technology (Moscow) and placed at our disposal by S. Bogatkov. M.p. is 191°C. The dependence of the alkaline hydrolysis kinetics on the additions of KCl up to ionic strength 1.0 at 25 and 50°C was studied by S.Bogatkov et al.[16].

For the technique of the kinetic measurements see Ref. 3.

Table 1

Rate Constants of the Alkaline Hydrolysis of Benzoates $C_6H_5COO(CH_2)_nN(CH_3)_3^+$ in the Presence of $NaClO_4$ and NaCl at 50° in Water. (Mean square error of arithmetic mean is given for k.

$10^3 c_{NaOH}$ M	c_{NaClO_4} M	k $M^{-1}.sec^{-1}$	$10^3 c_{NaOH}$ M	c_{NaCl} M	k $M^{-1}.sec^{-1}$
		n = 1			
1.21	1.00	12.43±0.42	1.21	1.00	20.97±0.78
1.21	4.00	6.28±0.33	1.21	3.24	15.54±0.55
1.21	5.29	4.83±0.24	1.21	4.00	13.25±0.59
			1.21	4.84	12.56±0.50
		n = 2			
2.25	-	3.76±0.11	4.51	0.0229	3.36±0.05
4.51	-	3.85±0.16	4.51	0.0617	2.88±0.07
4.51	1.00	0.881±0.072	4.51	0.0871	2.82±0.07
4.51	4.00	0.362±0.008	4.51	4.84	1.05±0.02
4.51	5.29	0.292±0.012	4.44	4.84	0.959±0.036
		n = 3			
4.85	-	0.925±0.023	22.6	0.0422	0.804±0.025
9.70	-	0.947±0.015	22.6	0.0806	0.652±0.032
24.2	-	0.896±0.017	24.2	0.249	0.585±0.025
24.2	1.03	0.255±0.005	24.2	1.00	0.461±0.009
24.2	4.05	0.0994±0.0031	24.2	4.00	0.338±0.014
22.6	5.29	0.0856±0.0040	22.6	4.84	0.332±0.006

The kinetic measurements were carried out under pseudo-monomolecular conditions at the high excess of NaOH. The second order rate constants were calculated by dividing the rate constants by the alkali concentration. The measurements were done in the presence of $NaClO_4$ and NaCl and at high concentrations of electrolyte ($\sqrt{\mu}$ = 1.0;2.0; and 2.3), since the main purpose of this work was to obtain reliable rate constants at $\sqrt{\mu}$ = 2.3. It should be said that our previous works compare the kinetic data just at $\sqrt{\mu}$ = 2.3

At each concentration of an electrolyte the measurements were repeated 4-6 times and aritmetic means of the obtained second order rate constants were calculated. Table 1 lists the corresponding values of k at various concentrations of $NaClO_4$ and NaCl.

It should be noted that the rate constants of the alkaline hydrolysis of 3-trimethylammoniumpropyl benzoate obtained in this work are about twice as high as those measured elsewhere [16] with KOH as an added neutral salt.

In Figs. 1,2, and 3 one can see the plots of the alkaline hydrolysis of formocholine - benzoate chloride choline - benzoate iodide, and 3-trimethylammoniumpropyl benzoate iodide vs. $\sqrt{\mu}$ in the presence of NaCl and $NaClO_4$.

Results and Discussion

For all alkyl benzoates studied $C_6H_5COO(CH_2)_nN(CH_3)_3^+$, negative salt effects in the presence of $NaClO_4$ are much higher than those with NaCl (see Figs. 1-3 and Table 2).

It has been found in Ref. 14 that negative salt effects of this reaction in the case of electroneutral substituents are also higher in the presence of $NaClO_4$ than with NaCl. At $\sqrt{\mu}$ = 2.3 for electroneutral substituents[14]:

$$\Delta lgk^{NaClO_4} = -0.08(\pm 0.04)\ lgk_o - 0.49(\pm 0.01) \quad (1)$$

$$\Delta lgk^{NaCl} = -0.09(\pm 0.03) lgk_o - 0.10(\pm 0.02) \quad (2)$$

where k_o is a rate constant at zero concentration of an

electrolyte.

It is natural to assume that with charged substituents the gross salt effect consists of the electrostatic effect Δlgk_{el}, and the specific component, $\Delta lg\ k_{sp}$, characteristic of compounds with electroneutral substituents. By subtracting the specific component, Δ^{lgk}_{sp}, from the overall salt effect, the values of electrostatic components of salt effects can be found for substrates with charged substituents:

$$\Sigma\Delta lgk^{x^{\pm}}_{js} - \Delta lgk^{x^{\pm}}_{j(sp)} = \Delta lg^{x^{\pm}}_{j(el)} \qquad (3)$$

where j denotes a reaction series. The general form of the equation for specific salt effect is :

$$\Delta lg\ k^{x}_{j(sp)} = a_{js}\ lgk^{x}_{jo} + b_{js} \qquad (4)$$

where s denotes a solution with a constant salt concentration.

Within the framework of the model used [17], in the case of charged substituents at high concentrations of electrolyte a substrate exists in the form of ion pairs and the over - all salt effect of substrates with a charged substituent should take into account the specific salt effect of ion pairs:

$$\Delta lg\ k^{x^{\pm}D^{\mp}}_{j(sp)} = a_{js}(lgk^{x^{\pm}}_{jo} + \Delta lgk_{j(el)}) + b_{js}, \qquad (5)$$

where $D^{\mp}$ denotes a counter-ion of a substituent $x^{\pm}$

From Eq. 5:

$$\Sigma\Delta lgk^{x^{\pm}} = lgk^{x^{\pm}}_{js} - lg\ k^{x^{\pm}}_{jo} = a_{js}(lgk^{x^{\pm}}_{jo} + \Delta lgk^{x^{\pm}}_{j(el)}) + \Delta lgk^{x^{\pm}}_{j(el)} + b_{js}$$

or

$$\Sigma\Delta lgk^{x^{\pm}}_{js} - a_{js}lgk^{x^{\pm}}_{jo} - b_{js} = (a_{js} + 1)\Delta lgk^{x^{\pm}}_{j(el)} \qquad (6)$$

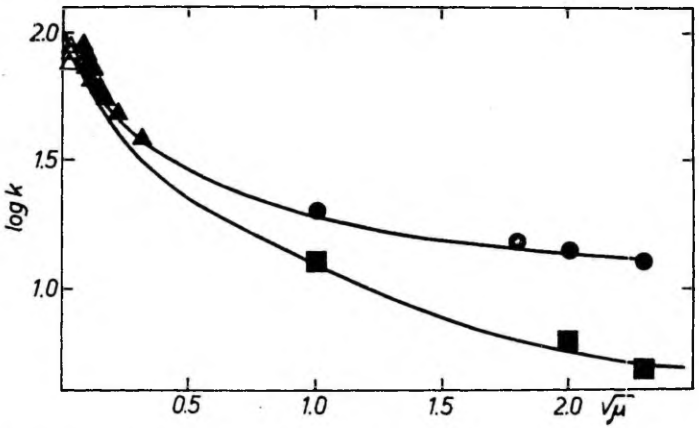


Fig.1. Plot of lgk of alkaline hydrolysis of formocholine-benzoate chloride vs. $\sqrt{\mu}$ at 50°C.

● - with NaCl
■ - with $NaClO_4$
▲ - with NaCl (Ref. 4)
Δ - without the neutral salt (Ref.4)

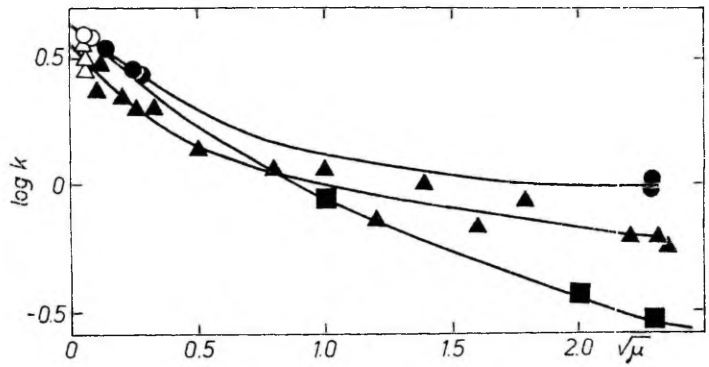


Fig.2. Plot of lg k of alkaline hydrolysis of choline-benzoate chloride vs. $\sqrt{\mu}$ at 50°C.

● - with NaCl
▲ - with NaCl (Ref.4)
■ - with $NaClO_4$
Light points denote measurements without the neutral salt.

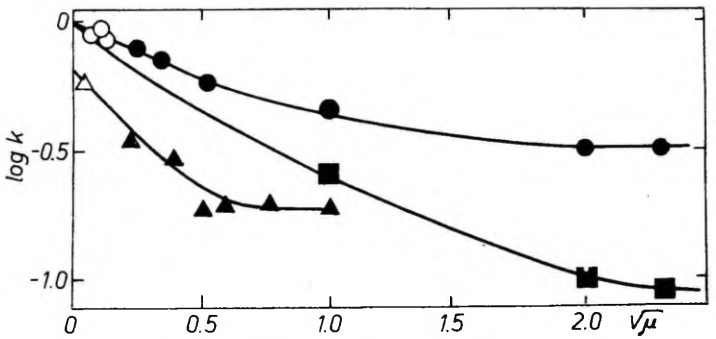


Fig. 3. Dependence of 3-trimethylammoniumpropyl benzoate iodide on $\sqrt{\mu}$ at 50°C.

● - with NaCl
■ - with $NaClO_4$
▲ - with NaCl (mean values by Ref. 16)
Light points denote measurements without a neutral salt.

By Eq. (6) one can calculate the values of electrostatic components of salt effects (Δlgk_{el}), if the over-all salt effect and parameters a and b in Eq. (4) for specific salt effects of the same reaction in the presence of the given neutral salt are known.

The values of Δlgk_{el} for the given charged substituent, calculated on the basis of salt effects in the presence of $NaClO_4$ and NaCl by Eq. (6), are essentially the same (see Table 2).

On the other hand, it is of interest to compare the experimental values of Δlgk_{el} and the theoretical values of the electrostatic effect [17]

$$\Delta lgk_{el} = \frac{QZ_1 Z_2}{r}$$

where Z_1 and Z_2 are reagent charges, r is a distance between charges in the transition state (in Å), $Q=e^2/2.3RT=3.21$

Table 2

Values of lgk_o, Slopes f, $\Sigma\Delta lgk$, Δlgk_{el} and Calculated Values of $\frac{QZ_1Z_2}{r}$ for Alkaline Hydrolysis of $C_6H_5COO(CH_2)_nN(CH_3)_3^+$ at 50°C

	n = 1*	n = 2*	n = 3*
lgk_o	2.05±0.03(4)	0.605±0.011	0.008±0.01
		0.542±0.040(4)	-0.20(16)
slope f	-1.31±0.17(4)	-0.54±0.07	-0.38±0.08
		-0.80±0.24(4)	-0.77±0.16(16)
change range	0.10 - 0.35	0.04-0.30	0.07-0.26
to calc. f		0.05-0.26(4)	0.07-0.51(16)
$-\frac{QZ_1Z_2}{r}$	1.34(16)	0.84 trans (16)	0.65 trans,trans
(model I[a])		1.17 gosh (16)	0.76 trans,gosh
$-\frac{QZ_1Z_2}{r}$	0.76	0.60 trans	0.48 trans,trans
(model II[b])		0.73 gosh	0.55 trans,gosh
	with $NaClO_4$		
$\Sigma\Delta lgk$	1.37	1.08	1.07
Δlgk_{el}	0.77	0.60	0.61
	with NaCl		
$\Sigma\Delta lgk$	0.95	0.56	0.48
		0.75(4)	
Δlgk_{el}	0.72	0.47	0.38
		0.65 [c]	
	with KCl		
$\Sigma\Delta lgk$[d]	-	-	0.48±0.17

* Ref. is given in parentheses

a) the degree of heterolysis of the C-O bond is close to unity[17]

b) the structure of the transition s-tate is close to that of an intermediate tetrahedral adduct, the degree of heterolysis of the C-O bond is close to zero [16].

c) calculated on the basis of $\Sigma\Delta lgk$(Ref.4)

d) specific salt effects are not studied.

at 50°C in water. However, the calculated values of lgk_{el} depend on the choice of structure of the transition state. In Ref. 17 the model was accepted according to which the degree of heterolysis of the C-O bond in the transition state is close to unity. The Δlgk_{el} values calculated by this model are close to experimental values of Δlgk_{max} for some interionic reactions. When studying salt effects of alkyl benzoates with charged substituents, Bogatkov[16] comes to conclusion that there is better agreement between the experimental data and the model suggesting that the structure of the transition state should be close to that of an intermediate tetrahedral adduct and the degree of heterolysis of the C-O bond in it should be close to zero.

The Δlgk_{el} values calculated by the two models are listed in Table 2.

As one can see from Table 2 our experimental data are in good agreement with the model from Ref. 16, according to which the structure of the transition state is close to that of an intermediate tetrahedral adduct.

Thus when determining the true values of electrostatic component, it is necessary to calculate a specific non-electrostatic effect of a neutral salt quantitatively. By subtracting the specific component from gross salt effect for charged substituents the true electrostatic components can be obtained. With different neutral salts they are essentially the same.

References

1. V. Maremäe, T. Püssa, and V. Palm, Reakts. sposobn. organ.soedin., 1. 127(1971)
2. V. Maremäe and V. Palm, Reakts. sposobn. organ.soedin., 2, 591(1971)
3. T. Püssa, V. Nummert(Maremäe), and V. Palm, Reakts. sposobn. organ.soedin., 9, 697(1972)
4. T. Püssa, V. Nummert(Maremäe), and V. Palm, 9,871(1972)

5. V. Nummert (Maremäe) and M. Uudam, Reakts. sposobn. organ.soedin., 10. 863(1973)
6. V. Nummert and V. Palm, Organic Reaktivity, 11, 579 (1975)
7. V. Nummert and M. Uudam, Organic Reactivity, 11, 599 (1975)
8. V. Nummert and I. Alakivi, Organic Reactivity, 11, 609 (1975)
9. V. Nummert and I. Alakivi, Organic Reactivity 11, 911 (1975)
10. V. Nummert and I. Alakivi, Organic Reactivity, 13, 105 (1976)
11. V. Nummert and I. Alakivi, Organic Reactivity, 4, 547 (1976)
12. V. Nummert and M. Piirsalu. Organic Reactivity, 14, 263 (1977)
13. V. Nummert, M. Piirsalu, and I. Alakivi, Organic Reactivity, 15, 133 (1978)
14. V. Nummert and M. Piirsalu, Organic Reactivity, 15, 240 (1978)
15. R.R. Renshaw and J.C. Ware, J. Am. Chem. Soc., 47, 2990 (1925)
16. S. Bogatkov, I. Kuplenskaya, and R. Romanova, Organic Reactivity, 11, 341 (1974)
17. V. Palm, V. Nummert, T. Püssa, M. Karelson, and I. Koppel, Reakts. sposobn. organ. soedin., 10, 223 (1973)

SOLVENT EFFECT ON THE DISTRIBUTION COEFFICIENTS V. THE EXTRACTION OF ACETIC AND PROPIONIC ACIDS FROM AQUEOUS PHASE BY ORGANIC SOLVENTS.

R.G.Makitra, Ya.N.Pirig, and D.I.Filtz.
Institute of Geology and Geochemistry of Fuels
Ac.Sci.Ukr.SSR, Lvov.

Received June 12, 1979

The distribution of acetic and propionic acids between water and 22 organic solvents was studied. The distribution obeys the Nernst-Shilov equation $lgK=nlgC_{org}-lgC_{aq}$. The values of "n" change from 0.6 (aniline) to 2.2 (cyclohexanone). The values of lgK correlate satisfactorily with the properties of solvents by a linear five-parameter equation.

In the previous communications[1,2] we showed that the distribution of carbonyl compounds, phenols and crotonic acid between two phases (aqueous and organic) may be described satisfactorily by means of a poly-paramater equation which takes into account the ability of organic phase to specific and unspecific solvation. Since the carbonic acid distribution processes are complicated by the association phenomena (mainly dimerization) in the organic phase and dissociation phenomena in the aqueous phase, it was interesting to verify tne applicability of the above equation for this case too.

In this paper we study the distribution of acetic acid and propionic acid between water and 22 organic solvents. In the literature there are numerous data about the extraction of these acids but, as a rule, for short series of solvents only.Besides,the results of different authors differ frequently for the same extragents considerably.There-

fore we have studied again the equilibrium distribution of these acids between water and a number of organic solvents.

EXPERIMENTAL

The solvents and the acids were purified by rectification and their properties are in accordance with the literature data. The experimental technique was as in Ref.[I] The calculations were done on a "Mir-2" computer.

RESULTS AND DISCUSSION

The equilibrium concentrations of acetic acid and their distribution between two phases are listed in Table I and corresponding concentrations of propionic acid are listed in Table 1. The distribution law of Nernst-Shilow $(C_{org})^n/C_{aq}=K$ is observed in the both cases over the concentration range studied. The corresponding values of K and n calculated by the least squares method are listed in Table 3 as well as their deviations, the correlation coefficients R, and the mean deviation s for the equations in the logarithmic form.

The logarithms of distribution constants of acids are correlated with the properties of solvents by means of a five-parameter equation of free energies, analogously as in Ref.[I]:

$$\lg K = A_0 + A_1 \frac{n^2-1}{n^2+2} + A_2 \frac{\varepsilon-1}{2\varepsilon+1} + A_3 \delta^2 + A_4 B + A_5 E$$

The properties of the used solvents and the correlated values of lgK for acetic and propionic acids are listed in Table 4. The data for dimethylaniline, dibenzyl ether, tricresylphosphate, and butylacetate N°N°I9-22 are not taken into account on calculations because the necessary parameters B and E for these solvents are absent in the literature.

Only a low correlation coefficient R=0.902 was obtained by means of treating the data for acetic acid by the above equation. But the value of R grows with excluding the data for two solvents from calculations: $CHCl_3$, N°2 (R=0.927) and ethylacetate N°5 (R=0.951); and this

Table I

EQUILIBRIUM CONCENTRATIONS OF DISTRIBUTION OF ACETIC ACID BETWEEN ORGANIC AND AQUEOUS PHASES MOLE/L.

C_{org}	C_{aq}
1. Benzene	
0.00074	0.0373
0.00147	0.0475
0.00210	0.0935
0.00232	0.1290
0.00289	0.1412
0.00336	0.1830
0.00420	0.2195
0.00442	0.2831
0.00484	0.3121
0.00526	0.336
0.00588	0.354
2. Chlorophorme	
0.00063	0.0131
0.00105	0.0258
0.00147	0.0569
0.00336	0.0884
0.00473	0.1055
0.00420	0.1230
0.00546	0.1765
0.00609	0.1919
0.0715	0.206
0.0183	0.266
0.0223	0.412
0.0570	0.545
3. n-Butanol	
0.0200	0.0244
0.0302	0.0372
0.0414	0.0512
0.0530	0.0642
0.0654	0.0768
0.0925	0.109
0.116	0.134
0.138	0.168
0.187	0.238
4. Cyclohexanone	
0.067	0.0140
0.0732	0.0165
0.0750	0.0224
0.098	0.043
0.102	0.035
0.109	0.054
0.118	0.068
0.135	0.078
0.151	0.090
0.154	0.083
0.157	0.098
5. Ethylacetate	
0.0132	0.0148
0.0212	0.0262
0.0302	0.0383
0.0402	0.0508
0.0500	0.0654
0.0618	0.0792
0.0742	0.0980
0.0940	0.1192
0.108	0.136
6. Anisole	
0.0012	0.0322
0.0030	0.0520
0.0046	0.0712
0.0054	0.0992
0.0062	0.1204
0.0074	0.1462
0.0156	0.2056
0.0210	0.276
0.0278	0.331
0.0348	0.460
0.0632	0.560
0.0724	0.900
7. Bromobenzene	
0.0012	0.089
0.0018	0.152
0.0020	0.249
0.0028	0.303
0.0038	0.377
0.0046	0.462
0.0052	0.523
8. Cyclohexylchloride	
0.0042	0.120
0.0062	0.191
0.0074	0.240
0.0092	0.302
0.0101	0.350
0.0110	0.362
0.0140	0.440
0.0161	0.490
9. Benzyl alcohol	
0.0512	0.0196
0.0622	0.0314
0.0704	0.0443

Table I (continued).

C_{org}	C_{aq}
0.0924	0.0562
0.1036	0.0768
0.1136	0.0902
0.1182	0.1316
0.1298	0.1456
0.1604	0.1656
10. Dichloroethane	
0.0012	0.0211
0.0024	0.0390
0.0032	0.0632
0.0036	0.0810
0.0042	0.1042
0.0051	0.1376
0.0060	0.1644
0.0070	0.1908
0.0078	0.2212
0.0092	0.2496
11. Cyclohexanol	
0.0114	0.0096
0.0220	0.0200
0.0322	0.0302
0.0453	0.0420
0.0594	0.0534
0.0722	0.0656
0.0956	0.0812
0.1100	0.0968
0.1321	0.1248
0.1464	0.1308
12. Benzonitrile	
0.0116	0.0344
0.0168	0.0512
0.0178	0.0684
0.0232	0.0904
0.0268	0.1136
0.0316	0.1381
0.0382	0.1550
0.0456	0.2002
0.0552	0.2264
13. Chlorobenzene	
0.0016	0.1424
0.0028	0.1910
0.0044	0.2492
0.0052	0.3052
0.0070	0.4204
0.0084	0.5200
0.0102	0.5600
0.0114	0.6160
14. Dibutyl ether	
0.00411	0.00216
0.00607	0.00499
0.0110	0.0104
0.01175	0.01136
0.01235	0.01288
0.01935	0.02102
0.02900	0.02512
0.02750	0.02396
0.0300	0.0336
0.0390	0.0387
15. Tributhylphosphate	
0.00200	0.00090
0.00384	0.00210
0.00596	0.00315
0.00820	0.00414
0.00962	0.00522
0.0120	0.00656
0.01568	0.00804
0.01884	0.00953
16. Nitrobenzene	
0.0042	0.00826
0.0048	0.01160
0.0062	0.01324
0.0090	0.0206
0.0130	0.0282
0.0158	0.0325
0.0173	0.0382
0.0196	0.0426
0.0215	0.0447
17. Quinoline	
0.00096	0.00152
0.00214	0.00282
0.00315	0.00394
0.00458	0.00499
0.00756	0.00764
0.00937	0.00910
0.01162	0.01004
0.01345	0.01180
18. Aniline	
0.00067	0.00474
0.00117	0.00707
0.00186	0.00907
0.00296	0.01004
0.00407	0.01278
0.00492	0.01570
0.00643	0.01900
0.00760	0.02142
0.00882	0.02668

Table I (continued).

C_{org}	C_{aq}
19. Dibenzyl ether	
0.0216	0.0412
0.0252	0.0782
0.0266	0.1028
0.0330	0.1524
0.0354	0.1904
0.0382	0.2522
0.0422	0.2966
0.0472	0.3726
20. Dimethylaniline	
0.00255	0.00415
0.00392	0.00693
0.00608	0.00962
0.00784	0.01240
0.0106	0.01515
0.0120	0.01815
0.0136	0.02104
0.0159	0.02515
0.0180	0.0274
0.0237	0.0339
21. Tricresylphosphate	
0.0032	0.0166
0.0050	0.0318
0.0062	0.0416
0.0118	0.0660
0.0212	0.0874
0.0240	0.1092
0.0322	0.1362
0.0402	0.1776
22. Butylacetate	
0.0064	0.0172
0.0098	0.0300
0.0136	0.0420
0.0185	0.0520
0.0198	0.0590
0.0258	0.0760
0.0306	0.0961
0.0366	0.1122
0.0564	0.1190

Table 2

EQUILIBRIUM CONCENTRATIONS OF DISTRIBUTION OF PROPIONIC ACID BETWEEN ORGANIC AND AQUEOUS PHASES MOLE/L

C_{org}	C_{aq}
1. Benzene	
0,0054	0.052
0.0078	0.078
0.0108	0.100
0.0142	0.125
0.0206	0.149
0.0242	0.172
0.0306	0.196
0.0422	0.235
2. Cyclohexanone	
0.0634	0.0112
0.0864	0.0152
0.1102	0.0202
0.1246	0.0258
0.1512	0.0316
0.1676	0.0380
0.1764	0.0436
0.2160	0.0503
0.2492	0.0574
0.2840	0.0708
3. Ethylacetate	
0.0200	0.0142
0.0322	0.0198
0.0494	0.0272
0.0628	0.0342
0.0808	0.0406
0.0916	0.0486
0.1162	0.0576
0.1404	0.0648
0.1616	0.0764
0.1836	0.0849
4. Anisole	
0.0078	0.0320
0.0148	0.0582
0.0194	0.0804
0.0272	0.0982
0.0396	0.1208
0.0488	0.1512
0.0552	0.1714
0.0828	0.2532
0.0888	0.2674

Table 2 (continued)

C_{org}	C_{aq}	C_{org}	C_{aq}	C_{org}	C_{aq}
5. Bromobenzene		0.0744	0.1922	0.0192	0.1772
0.0020	0.0518	0.0844	0.2352	0.0248	0.2104
0.0032	0.0692	8. Dichloroethane		0.0370	0.2280
0.0048	0.0856	0.0020	0.0178	11. Tributylphosphate	
0.0058	0.0964	0.0040	0.0332	0.0272	0.0044
0.0060	0.1024	0.0072	0.0512	0.0582	0.0096
0.0074	0.1204	0.0114	0.0692	0.1022	0.0163
0.0114	0.1624	0.0134	0.0856	0.1254	0.0232
0.0122	0.1663	0.0174	0.1096	0.1842	0.0282
0.0182	0.2062	0.0242	0.1392	0.2214	0.0362
0.0258	0.2514	0.0302	0.1594	0.2612	0.0442
0.0344	0.3012	0.0354	0.1863	0.2916	0.0564
0.0480	0.3514	0.0508	0.2390	0.3512	0.0628
6. Cyclohexylchloride		9. Benzonitrile		12. Quinoline	
0.0036	0.0322	0.0137	0.0078	0.0158	0.0158
0.0048	0.0508	0.0244	0.0192	0.0260	0.0182
0.0078	0.0744	0.0336	0.0264	0.0554	0.0306
0.0106	0.1028	0.0516	0.0436	0.0572	0.0312
0.0124	0.1248	0.0644	0.0520	0.0708	0.0352
0.0166	0.1484	0.0742	0.0576	0.0920	0.0398
0.0184	0.1662	0.0844	0.0688	0.1216	0.0482
0.0220	0.1964	0.0984	0.0766	0.1710	0.0598
0.0250	0.2206	0.1128	0.0984	0.2340	0.0748
7. Benzyl alcohol		0.1342	0.1084	13. Aniline	
0.0150	0.0501	10. Chlorobenzene		0.0052	0.0168
0.0204	0.0702	0.0010	0.0234	0.0126	0.0322
0.0304	0.0904	0.0018	0.0412	0.0220	0.0468
0.0372	0.1028	0.0042	0.0612	0.0332	0.0608
0.0424	0.1324	0.0062	0.0788	0.0502	0.0764
0.0528	0.1436	0.0098	0.1084	0.0652	0.0924
0.0584	0.1640	0.0128	0.1184	0.0804	0.1012
0.0660	0.1784	0.0160	0.1432	0.0992	0.1203

Table 2 (continued)

C_{org}	C_{aq}	C_{org}	C_{aq}	C_{org}	C_{aq}
0.I200	0.I364	0.0I22	0.0560	0.0468	0.I902
0.I364	0.I536	0.0I88	0.0766	0.0600	0.2I74
I4.Dimethylaniline		0.0246	0.I040	0.08I2	0.2520
0,0024	0.0I76	0.0304	0.I292	0.0896	0.2862
0.0074	0.0388	0.0400	0.I502		

Table 3

PARAMETER OF DISTRIBUTION EQUATIONS OF ACETIC AND PROPIONIC ACIDS BETWEEN ORGANIC SOLVENTS AND WATER

N°	Solvent	K	n	R	s
I	Benzene	0.0058±0.00II	I.208±0.075	0.98I	0.065
2	Chloroforme	0.II7±0.0I87	0.8I0±0.067	0.964	0.I30
3	n-Butanol	0.9II5±0.0328	0.95I±0.027	0.996	0.082
4	Cyclohexanone	0.I76I±0.0300	2.I83±0.I76	0.969	0.075
5	Ethylacetate	0.684I±0.0I67	I.049±0.0I8	0.999	0.0I5
6	Anisole	0.II55±0.0I03	0.872±0.046	0.984	0.079
7	Bromobenzene	0.0044±0.00I4	I.I45±0.I23	0.972	0.070
8	c-Hexylchloride	0.0237±0.0025	I.06I±0.050	0.993	0.025
9	Benzyl alcohol	0.I549±0.02I9	I.926±0.I37	0.983	0.063
I0	Dichloroethane	0.0084±0.00I0	I.300±0.052	0.994	0.042
II	Cyclohexanol	I.0834±0.0226	I.009±0.0I6	0.999	0.0I7
I2	Benzonitrile	0.III7±0.0II4	I.233±0.064	0.99I	0.040
I3	Chlorobenzene	0.0485±0.0053	0.789±0.048	0.989	0.037
I4	Dibutyl ether	0.0672±0.0064	I.III±0.052	0.99I	0.050
I5	Tributylposphate	I.7340±0.0597	I.042±0.030	0.998	0.026
I6	Nitrobenzene	0.0488±0.0035	0.988±0.036	0.995	0.028
I7	Quinoline	I.8I60±0.0270	0.77I±0.0II	0.999	0.0I2
I8	Aniline	0.0946±0.0489	0.623±0.034	0.990	0.036
I9	Dibenzyl ether	0.0004±0.000I	2.830±0.I92	0.984	0.063
20	Dimethylaniline	0.0863±0.0038	0.937±0.022	0.998	0.020
2I	Tricresylphosph.	0.3882±0.0407	0.845±0.054	0.988	0.059
22	Butylacetate	0.2809±0.0II0	I.046±0.023	0.998	0.0I9

Table 3 (continued)

№	Solvent	K	n	R	s
		Propionic acid			
I	Benzene	0.4204±0.0275	0.7II±0.086	0.992	0.029
2	Cyclohexanone	2.8739±0.0962	I.259±0.039	0.996	0.024
3	Ethylacetate	3.0376±0.0537	0.8I5±0.0I5	0.999	0.0I4
4	Anisole	0.4950±0.0I96	0.845±0.026	0.997	0.026
5	Bromobenzene	0.3904±0.0083	0.629±0.0I0	0.999	0.0I4
6	c-Hexylchloride	0.I3I3±0.008I	0.954±0.08I	0.996	0.026
7	Benzyl alcohol	0.5445±0.0228	0.854±0.030	0.995	0.022
8	Dichloroethane	0.3699±0.0089	0.804±0.0I3	0.999	0.0I7
9	Benzonitrile	0.9308±0.0470	I.I30±0.039	0.995	0.037
I0	Chlorobenzene	0.5003±0.0234	0.636±0.02I	0.995	0.033
II	Tributylphosph.	5.4834±0.I570	I.037±0.03I	0.997	0.032
I2	Quinoline	6.I688±0.2320	0.58I±0.03I	0.990	0.0I6
I3	Aniline	I.8I76±0.0290	0.654±0.0II	0.999	0.0I6
I4	Dimethylaniline	0.5I80±0.0I53	0.788±0.0I8	0.998	0.027

is a region of a satisfactory correlation[4]. The dependence of acetic acid distribution constant between water and organic phase on its properties is described by the equation:

$$\lg K = -3.671 + 2.941\,\frac{n^2-1}{n^2+2} + 4.745\,\frac{\varepsilon-1}{2\varepsilon+1} - 10.79\,\delta^2 + 0.00435B + 0.0850E;\ R=0.958;\ s=0.303;\ r_{01}=0.235;$$

$$r_{02}=0.491;\ r_{03}=0.143;\ r_{04}=0.844;\ r_{05}=0.462.$$

From the values of pair correlation coefficients and regression coefficients one can see that the most significant parameter with the greatest influence on acetic acid distribution process is the basicity, i.e.the acid-base interaction (the nucleophilic solvation of CH_3COOH) is of main importance, but other kinds of solvation increase the K value significantly, with the exception of the cohesion energy density of the organic phase which lowers the value of K. With excluding some parameters (see Ref.5) the correlation becomes considerably worse and with excluding the basicity

Table 4

LOGARITHMS OF DISTRIBUTION CONSTANTS BETWEEN ORGANIC PHASE AND WATER FOR ACETIC (K_1) AND PROPIONIC (K_2) ACIDS AND SOLVENT PARAMETERS

N°	Solvent	$\lg K_1$	$\lg K_2$	$\frac{n^2-1}{n^2+2}$	$\frac{\varepsilon-1}{2\varepsilon+1}$	δ^2	B	E
I	Benzene	-2.2366	-0.3762	0.2947	0.23I	0.085	48	2.I
2	Chloroforme	-0.93I4	-	0.2653	0.359	0.088	I4	3.28
3	n-Butanol	-0.0262	-	0.242I	0.457	0.I08	23I	I0.3
4	Cyclohexanone	-0.7542	0.4585	0.2699	0.46I	0.I04	242	0.5
5	Ethylacetate	-0.I649	0.4825	0.2275	0.385	0.082	I8I	I.6
6	Anisole	-0.9374	-0.3054	0.3030	0.344	0.097	I55	I.4
7	Bromobenzene	-2.3565	-0.4085	0.3232	0.373	0.096	40	0
8	Cyclohexylchloride	-I.6253	-0.88I7	0.27I5	0.408	0.074	40	/0/
9	Benzyl alcohol	-0.8099	-0.2639	0.3I36	0.0448	0.I69	208	I0.9
I0	Dichloroethane	-2.0757	-0.43I9	0.266I	0.43I	0.I08	40	0
II	Cyclohexanol	-0.0348	-	0.4408	0.452	0.I24	242	/6.2/[a]
I2	Benzonitrile	-0.95I9	-0.03II	0.3084	0.47I	0.I28	I55	0
I3	Chlorobenzene	-I.3I42	-0.3008	0.3064	0.377	0.087	38	0
I4	Dibutyl ether	-I.I726	-	0.242I	0.289	0.06I	285	0
I5	Tributylphosphate	-0.2390	0.7890	0.2560	0.470	0.040	280	2.4
I6	Nitrobenzene	-I.3II6	-	0.3I98	0.479	0.II3	67	0
I7	Quinoline	-0.2592	0.7902	0.3525	0.423	0.II3	494	0
I8	Aniline	-0.024I	0.2595	0.3353	0.398	0.I2I	346	6.2

[a]) The value of "E" was taken for Et_2CHOH

parameter the correlation is destroyed. The following values of R were obtained for the four-parameter equation with excluding some parameters: 0.947; 0.891; 0.929; 0.728; 0.913. The dependence $y' = lgK-f(n)-f(\varepsilon)+f(\delta^2) = f(B)$ is illustrated in Fig.1.

Similar results were also obtained for propionic acid.The correlation for all 13 solvents studied is unsatisfactory (R=0.918) but with excluding the data for cyclohexylchloride (N°8), the correlation becomes satisfactory for the remained 12 points: $lgK = 0.788 - 4.016\frac{n^2-1}{n^2+2} + 0.670\frac{\varepsilon-1}{2\varepsilon+1} - 3.618\delta^2 + 0.00312B - 0.0134E$ with R=0.976, s=0.137, and pair correlation coefficients r_{01}=0;153; r_{02}=0.459; r_{03}= =0.300; r_{04}=0.833; r_{05}=0.058. Fig.2 illustrates the dependence $y' = lgK+f(n)-f(\varepsilon) + f(\delta^2)+f(E)$.

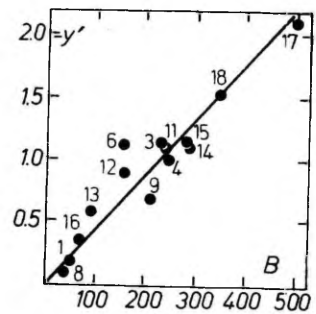


Fig.1.The dependence $y' = lgK-f(n)-f(\varepsilon)+f(\delta^2)=f(B)$ for acetic acid distribution

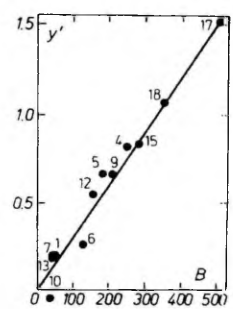


Fig.2.The dependence $y'= lgK+f(n)-f(\varepsilon)+f(\delta^2)+f(E)= f(B)$ for propionic acid distribution

In contrast to acetic acid for propionic acid the value of lgK is increased by the basicity (the most significant parameter) and polarity only and the other parameters decrease these value. The process of exclusion of some parameters in accordance with Ref.5 indicates that the polarity and electrophilicity are insignificant and, as a result, the propionic acid distribution may be described by the following

four or three-parameter equations:

$$\lg K = I.I39 - 4.655\,\frac{n^2-1}{n^2+2} - 2.824\,\frac{\varepsilon-1}{2\varepsilon+1} + 0.00331B - 0.0I69\,E$$

R=0.973; s=0.I46.

$$\lg K = 0.704 - 3.598\,\frac{n^2-1}{n^2+2} + 0.822\,\frac{\varepsilon-1}{2\varepsilon+1} - 4.688\,\delta^2 + 0.00302\,B$$

R=0.973; s=0.I49

$$\lg K = I.I33 - 4.29I\,\frac{n^2-1}{n^2+2} - 4.0I2\,\delta^2 + 0.00322\,B$$

R= 0.969; s=0.I36.

These investigations confirm the applicability of the five-parameter equation, which takes into account various kinds of interaction in solvents, for describing the carboxylic acid distribution processes between water and organic phases. The proposed equation enables to calculate the values of K by the known properties of solvents. But it should be noted that a solvent with the maximum value of K is not always the best industrial extragent of acids from aqueous solutions. Unlike the described in the previous communications phenols and carbonyl compounds, the acids are able to dissociate and associate in the solvents which is indicated by the "n" values different from unity. As a result, the calculated by the above equations values of "K" will be equal to the experimental values of "K" only at $n \simeq 1$ or when the term $n\lg C_{org}$ in the equation $\lg K = n\lg C_{org} - \lg C_{aq}$ will be equal to zero, i.e. at $C_{org}=1$ and $K=1/C_{aq}$. It is necessary to emphasize that the attempts to correlate the values of "n" with the properties of solvents are unsuccessful.

From these data one can see that with acetic acid the maximum values of constants are for quinoline (K=1.82), tributylpnosphate (K=1.7), cyclohexanol (K=1.08), and n-butanol (K=0.91) and minimum values are for hydrocarbons, halogenhydrocarbons, and ethers. The low values of constants ca.0.09 are observed for amines- aniline and dimethylaniline. But the actual extraction depends also on the "n" values. The maximum value of "n" (2.18) is observed for cyclohexanone; ether ($n \simeq 2.8$) and benzyl accohol ($n \simeq 1.93$) also have high "n" values, but the extraction with these solvents is unexpedient due to the low "K" values. The high values of

"n" indicate almost complete dimerization or partial trimerization of acetic acid in these solvents. The appreciable dimerization takes place also in dichloroethane ($n \simeq 1.3$), benzonitrile ($n \simeq 1.25$), and benzene ($n \simeq 1.2$).

Such dependences are also observed for propionic acid, but in this case the values of "K" are higher and those of "n" are lower and in most cases $n < 1$.

The best extragents for acetic acid are cyclohexanone (the ratio C_{org}/C_{aq} changes with the increase in the dissolved acid concentration from ca.5 to 1.6) and especially tributylphosphate ($C_{org}/C_{aq} \simeq 2$). For other solvents the concentration ratios are not so favorable; in our case it is close to 1 (butanol, ethylacetate, benzyl alcohol, cyclohexanol, dibutyl ether, quinoline) or even considerably lower. It is clear that for propionic acid the concentration of the acid in the organic phase is higher but the order of solvent effectivities is the same. The best extragents are cyclohexanone and tributylphosphate ($C_{org}:C_{aq} \simeq 5$).

References

1. R.G.Makitra, Ya.N.Pirig, A.M.Zeliznyj, M.A.Daniel de Aguar, V.L.Mikolajev, and V.A.Romanov, Organic Reactivity I4, 421 (1977).
2. R.G.Makitra and Ya.N.Pirig, Organic Reactivity, I5, 547 (1978).
3. Ya.M.Pavlovskaya, A.K.Charikov and V.I.Tikhomirov, Zh. obsh.khim., 47, 536 (1975).
4. V.A.Palm. Fundamentals of Quantitative Theory of Organic Reactions. "Khimiya", L.1977, p.315.
5. N.B.Chapman, M.R.J.Dack, D.J.Newman, J.Shorter, and R.Wilkinson. J.Chem.Soc.1974, Perkin Trans.p.II, 962.

SOLVENT EFFECTS ON THE DECOMPOSITION RATE OF PEROXYDES

N.S. Tsvetkov, V.Ya. Shukovskij, R.G. Makitra, and Ya.N. Pirig.

I. Franko State University, Lvov
Institute of Geology and Geochemistry of Fuels AN Ukr.SSR

Received June 12, 1979

The solvent effects on the rate of thermal decomposition of peroxyformic acid tert-butyl ester and the reactions of dimerization of 2,4,6-triphenylphenoxy-radicals and dissociation of the peroxy compound are satisfactorily described by the following five-parameter equation: $\lg k = A_0 + A_I f(n) + A_2 f(\varepsilon) + A_3 \delta^2 + A_4 B + A_5 E$.

The solvent effects on the rates of chemical reactions is one of the most important problems in the chemical kinetics. Ref[1] shows, using many examples, that for the heterolytic reactions in general case the lgk value depends on the specific and non-specific solvation factors. The influence of solvents on the rate of radical reactions is studied considerably less; in this respect the reactions of oxydation of organic compounds[2] are studied best of all.

In the previous paper[3] we showed that the four-parameter Koppel-Palm equation:

$$\lg k = A_0 + A_I f(n) + A_2 f(\varepsilon) + A_3 B + A_4 E$$

is suitable for the description of solvent effects on the polymeric azelainic acid peroxyde thermal decomposition rate, the polarity and basicity of a solvent being the only significant parameters. The regression coefficient signs at these parameters are positive, i.e. the solvation of a compound in activated state occurs or otherwise the solvation favors the decomposition of the molecule, apperently, due to the O-O bond weakening.

It was interesting to verify the applicability of the above equation to describe solvent effects on the decomposition of other peroxy compounds. With that end in view we studied the experimental data [4,5] on the decomposition of tert-butyl peroxyformat in the presence of pyridine and on the reversible recombination of 2,4,6-triphenylphenoxyl radicals. The corresponding values of lgk and solvent parameters are listed in Tables I and 2.

From the data of Ref.[4] we excluded the results for the decomposition in diphenylmethane and styrene, since for these solvents the numeric values of basicity "B" and electrophilicity "E" are absent; for many other solvents the values of B and E are accepted to be the same as for their nearest homologues (these values for E are given in paramtheses and for B are marked in notes). The calculation results for remained 18 solvents are excellently correlated by the following four-parameter equation:

$$\lg k \cdot 10^3 = -3.429 + 4.247\,\frac{\varepsilon - 1}{2\varepsilon + 1} + 8.738\,\frac{n^2-1}{n^2+1} + 0.00078B +$$

$$+ 0.171E \text{ with } R=0.994,\ s=0.042,$$

and the pair correlation coefficients $r_{01}=0.862$, $r_{02}=0.275$, $r_{03}=0.059$, and $r_{04}=0.484$.

With excluding some parameters according to Ref.[6] the values of the correlation coefficient decrease to 0.796; 0.909; 0.937, and 0.900. Thus both the values of pair correlation coefficients and the treatment as in Ref.6 indicate the neglible significance of the basicity parameter. The decomposition process of perester $HC(O)O\text{-}OC(CH_3)_3$ may be satisfactorily described by a three-parameter equation:

$$\lg k \cdot 10^3 = -3.056 + 4.348\,\frac{\varepsilon - 1}{2\varepsilon + 1} + 7.824\,\frac{n^2-1}{n^2+1} + 0.165E$$

with $R=0.987$ and $s=0.105$. The dependence $y'=\lg k \cdot 10^3 - 7.824f(n) - 0.165E = f(\varepsilon)$ is illustrated in Fig. I.

The same data from Ref.[4] for 13 solvents were verified in Ref.[7] on the one-parameter correlation with the Reichardt electrophilicity parameter E_T but low correlation coefficient $R = 0.929$ was obtained only. Thus the inclusion of

Table I

RATE CONSTANTS FOR DECOMPOSITION OF $HC^{O}_{OO}\text{-}C(CH_3)_3$ IN THE PRESENCE OF PYRIDINE IN SOME SOLVENTS ([illegible].*) AND THE PARAMETER OF SOLVENTS

N°	Solvent	$k \cdot 10^3$ $mole^{-1} \cdot sec^{-1}$	$\lg k_{+3}$	$\frac{\varepsilon-1}{2\varepsilon+1}$	$\frac{n^2-1}{n^2+1}$	B	B
I	Nitrobenzene	212	2.3263	0.4147	0.4788	67	0
2	Nitromethane	167	2.2227	0.3126	0.4808	65	5.1
3	Dichloromethane	69	1.8388	0.3398	0.4217	23	2.7
4	Chloroforme	45.2	1.6551	0.3357	0.3587	[illegible]	3.28
5	Chlorobenzene	40.9	1.6117	0.3968	0.3775	38	0
6	p-Chlorotoluene	39.7	1.5988	0.3954	0.3860	38*	(0)
7	Tetrahydrofurane	30.8	1.4886	0.3292	0.4049	287	[illegible]
8	Dioxane	23.0	1.3617	0.3385	0.2231	237	4.2
9	Benzene	21.5	1.3324	0.3852	0.2306	48	2.1
10	Toluene	17.7	1.2480	0.3829	0.2395	58	1.3
11	Cumene	15.1	1.1790	0.3806	0.2396	56	(1)
12	p-Xylene	13.7	1.1367	0.3822	0.2292	68	(1)
13	p-Cymene	11.7	1.0682	0.3791	0.2277	60**	(1)
14	Dibutyl ether	7.01	0.8457	0.3239	0.2893	285	0
15	CCl_4	6.08	0.7839	0.3615	0.2261	0	0
16	Cyclohexene	3.79	0.5786	0.3531	0.2243	97	(0)
17	Cyclohexane	2.11	0.3222	0.3408	0.2027	0	0
18	n-Heptane	1.52	0.1818	0.3164	0.1906	0	0

*) The value for chlorobenzene

**) The value for t-Butylbenzene

the non-specific solvation into calculations by means of multiparameter equation improves the correlation considerably.

Positive sign of the regression coefficient at the all equation terms indicates that both the specific and non-specific solvation favors the O-O bond breaking and the decomposition of the molecule. The role of the electrophilic solvation comes probably to the formation of a donor-acceptor complex

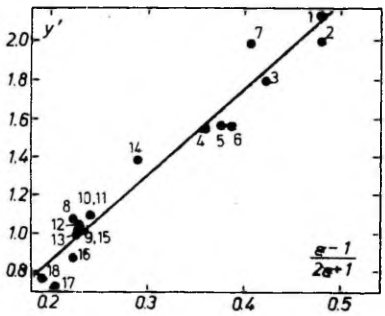


Fig.1. The dependence $y' = \lg k \cdot 10^3 + 3.056 - 7.824 f(n) - 0.165 E = f(\varepsilon)$ for thermal decompostion of $H\overset{O}{\underset{OO}{\sim}}C(CH_3)_3$.

between the solvent and peroxyde through the carbonyl group oxygene and, as a result, the weakening of O-O bond. Previously we showed that enanthyl peroxyde formed a complex with the weak electron acceptor CCl_4[8]. In Ref.[9] the authors show spectrophotometrically that the peroxydes interact with the electrophilic solvents such as alcohols. Indeed, the maximum rate of decomposition there is observed in accepting solvents such as nitromethane, nitrobenzene, CH_2Cl_2, $CHCl_3$. However, the non-specific solvation is also of important role for activation of molecule. This is confirmed by significant decrease in the R value when these terms are excluded and by the high pair correlation coefficient on polarizability r=0.863.

It should be noted that solvation favors the decomposition of both perester $HC\overset{O}{\underset{OO}{\sim}}C(CH_3)_3$ and polymeric peroxyde of azelainic acid, but in the first case the main influence is exerted by the polarizability and electrophilicity of a solvent and in the second case by the polarity and basicity which may be accounted for by different character of the groups $R-C\overset{O}{\underset{O-O}{\sim}}R'$ and $R-C\overset{O}{\underset{O-O}{\sim}}C\overset{O}{\underset{R'}{\sim}}$, and, as a result, the different character of their solvation.

The linear multiparameter equation works also for the description of the solvent effects on the rate of reversible reactions of dimerization of 2,4,6-triphenylphenoxy radicals and the dissociation of the obtained dimer[5]:

$$2\ PhO^{\bullet} \underset{2\ k_{-I}}{\overset{2\ k_I}{\rightleftharpoons}} D$$

Table 2

LOGARITHMS OF RATE CONSTANTS OF DIMERIZATION ($k.10^{-7}$ mole/l-sec) AND DISSOCIATION ($k.10^{-3}$ sec^{-1}) OF TRIPHENYLPHENOXY RADICALS (Ref.[5]) IN SOME SOLVENTS AND THEIR PARAMETERS

N°	Solvent	lgk_I	lgk_{-I}	$lgK.10^5$	$\frac{n^2-1}{n^2+2}$	$\frac{\varepsilon-1}{2\varepsilon+1}$	δ^2	B	E
I	Hexane	I.7324	0.204I	-0.5229	0,2289	0.I85	0.054	0	0
2	CCl_4	I.2430	0.2430	0.0000	0,2742	0.225	0.076	0	0
3	Toluene	0.845I	0,3222	0.477I	0.2926	0.238	0.080	58	I.3
4	Benzene	0.8I29	0.4I50	0.602I	0.2947	0.23I	0.085	48	2.I
5	Dioxane	0.2788	0.477I	I.204I	0.2453	0.223	0.IIO	237	4.2
6	Chlorobenzene	0.04I4	0.30I0	I.3424	0.3064	0.377	0.087	38	0
7	Chloroforme	-0.30I0	0.04I4	I.3424	0.2667	0.359	0.088	I4	3.3
8	Pyridine	-0.6576	-0.2696	I.3979	0.2989	0.44I	0.I04	472	0
9	Dimethylformamide	-0.2228	0.I46I	I.I76I	0.2584	0.488	0.I2I	3I9	2.6
I0	tert-Butanol	0.2430	-0.2798	0.477I	0.234I	0.434	0.II3	247	9.0
II	Acetonitrile	0.4I50	0.4624	I.04I4	0.2II9	0.480	0.I52	I60	5.2
I2	i-Propanol	0.7404	0.2I75	0.477I	0.2302	0.460	0.I37	236	8.7
I3	n-Butanol	0.7924	0.3979	0.602I	0.2400	0.458	0.II2	230	I0.8
I4	n-Propanol	0.9085	0.5052	0.602I	0.2344	0.455	0.I37	237	I0.6
I5	Ethanol	0.9345	0.4I50	0.477I	0.22I4	0.469	0.I58	235	II.6
I6	Methanol	0.7782	0.6233	0.845I	0.2033	0.477	0.I96	2I8	I4.9
I7	Glycole	o.I76I	-0.3468	0.477I	0.2592	0.483	0.3I8	224	I5.0

and on the value of equilibrium constant of this reaction, "K", though the obtained correlation in this case is worse than in the previous case. The authors of Ref.[5] tried to correlate the lgk_1 value with the Reichardt electrophilicity parameter E_T^7 which includes partially the nonspecific solvation factors [10] and established the presence of a V-like dependence. Hydrocarbons and halogenohydrocarbons yield to the same branch of the dependence where with increase in E_T the rate decreases and in polar solvents - alcohols, acetone, dimethylformamide-the dimerization rate increases with increase in E_T. The minimum rate is observed in pyridine. However, many solvents (glycole, ethanol, methanol) do not fit the obtained dependence at all. The authors of Ref.[5] explain the low values of k in $CHCl_3$ and pyridine as a result of specific solvation by these solvents. But the character of the solvation by donor pyridine and by acceptor $CHCl_3$ should differ.

An attempt to correlate the data from Ref.[5] all by the five-parameter equation which includes (besides polarizability, polarity, basicity, and electrophilicity parameters) the density of cohesion energy:

$$lgk = A_0 + A_I \frac{n^2-1}{n^2+2} + A_2 \frac{\varepsilon-1}{2\varepsilon+1} + A_3\delta^2 + A_4B + A_5E$$

leads to an unsatisfactory correlation coefficient R=0.847. But with exclusion from the consideration three points: $CHCl_3$ (N°7), dioxane (N°5) and tert-butanole (N°10) the R-value grows up to 0.942; 0.978, and 0.981, respectively, i.e. is in the region of good correlation. The equation is obtained:

$$lgk.10^{-7} = 4.693 - 8.660\frac{n^2-1}{n^2+2} - 4.294\frac{\varepsilon-1}{2\varepsilon+1} - 3.562\,\delta^2 - 0.00099IB + 0.073E$$

with R=0.981, s=0.151 and pair correlation coefficients $r_{01}=0.411$; $r_{02}=0.562$; $r_{03}=0.267$; $r_{04}=0.682$, and $r_{05}=0.777$.

The negative signs of regression coefficients at all the parameters (with the exception of electrophilicity) indicate that both non-specific and nucleophilic solvation stabilize

the radical and hinder the reaction of its dimerization and the electrophilic solvation favors the dimerization which corresponds to the right branch of V-like plot $\lg k_1$ vs. E_T[5]. The presence of the V-like dependence is, apparently, due to the summation of the opposite tendencies of solvent effects.

Excluding separate parameters in turn as in Ref.[6], one obtains five four-parameter equations with R=0.921; 0.910; 0.960; 0.973; and 0.932, respectively. Thus the basicity parameter "B" and the cohesion energy density are of least significance. Are they excluded, we obtain the following equations:

$$\lg k \cdot 10^{-7} = 5.III - 9.404\,\frac{n^2-1}{n^2+2} - 5.446\,\frac{\delta^2-1}{2\delta^2+1} - 3.295\delta^2 + 0.075E.\quad R=0.973;\ s = 0.170$$

$$\lg k \cdot 10^{-7} = 5.478 - II.183\,\frac{n^2-1}{n^2+2} - 5.838\,\frac{\delta^2-1}{2\delta^2+1} + 0.043E.\quad R = 0.954;\ S = 0.209.$$

The five parameter linear equation is also suitable for the description of solvent influence on the backward reaction of dissociation of peroxyde ($\lg k_{-1}$) and the equilibrium constant of reaction $\lg K = \lg k_1/k_{-1}$ too. But the correlation in this case is worse which is caused, probably, by the less accuracy of determining k_{-1} value (according to[5] the error of determining k_1 equals $\pm 20\%$ and of k_{-1} $\pm 50\%$). Correlation coefficient R for 14 points (points N°N°5,7,10 are excluded) equals R=0.916 and after additional excluding point N°12 (isopropanol) R grows to 0.939 only which corresponds to a "bad" correlation. For 13 points we obtained the following equations:

$$\lg k \cdot 10^{-3} = 0.234 - 0.197\,\frac{n^2-1}{n^2+2} + 0.934\,\frac{\delta^2-1}{2\delta^2+1} - 1.253\delta^2 - 0.00145B + 0.0326E;\quad R=0.939;\ s=0.097.$$

$$\lg k \cdot 10^{5} = -3.397 + 10.02\,\frac{n^2-1}{n^2+2} = 4.355\,\frac{\delta^2-1}{2\delta^2+1} - 2.226\delta^2 + 0.000IB + 0.0027E;\quad R=0.911;\ s=0.271.$$

For the first equation polarizability is a negligible parameter, for the second - the basicity. Finally the process of dissociation may be described satisfactorily by the

following equation:

$$\lg k \cdot 10^{-3} = 0.179 + 0.956 \frac{\varepsilon - 1}{2\varepsilon + 1} - 1.303\,\delta^2 - 0.00147B + 0.0337E;\ R = 0.939;\ s = 0.097$$

and

$$\lg K \cdot 10^{5} = -3.438 + 10.094 \frac{n^2 - 1}{n^2 + 2} + 4.468 \frac{\varepsilon - 1}{2\varepsilon + 1} - 2.251\,\delta^2 + 0.0025E;\ R = 0.911;\ s = 0.271.$$

Thus on the examples of thermal decomposition of polymeric peroxyde of azelainic acid[3] and tert-butylperformate and the reversible dimerization-dissociation of triphenylphenoxyl radicals we have shown that the five-parameter linear equation can be applied for the description of solvent effects on the rate of radical processes.

L I T E R A T U R E

1. I.A.Koppel and V.A.Palm in "Advances in Linear Free Energy Relationships", Plenum Press, London, 1972, p.265.
2. S.G.Entelis and R.P.Tiger, Kinetics of Reactions in Liquid Phase. M., "Khimiya", 1975.
3. N.S.Tsvetkov, V.Ya.Shukovskij, R.G.Makitra, and Ya.N.Pirig, Organic Reactivity 15, 68 (1978).
4. R.E.Pincock, J.Am.Chem.Soc. 86, 1820 (1964); 87, 1274 (1965).
5. P.P.Levin, I.V.Khudyakov, I.A.Khardina, and L.N.Rygalov, Izv.AN USSR, ser.khim., 1977, N°11, 2605.
6. N.B.Chapman, M.R.J.Dack, D.J.Newman, J.Shorter, and R.Wilkinson, J.Chem.Soc. 1974, Perkin Trans.p.II.962.
7. Ch.Reichardt, K.Dimroth, Losungsmittel und empirische Parameter zur Charakterisierung ihrer Polaritat, in "Fortschritte der chemischen Forschung", II, N°1, 556 (1968).
8. R.G.Makitra, L.I.Ivanyk, and V.L.Mizyuk, Izv.vuz.USSR, Khimija i khim.technol. 18, 326 (1975).
9. A.A.Turovskij and R.V.Kutsher, Zh.phis.khim. 47, 9 (1973)
10. I.A.Koppel and A.I.Paju. Organic Reactivity, 11, 139 (1974).

Rbl. 1.10